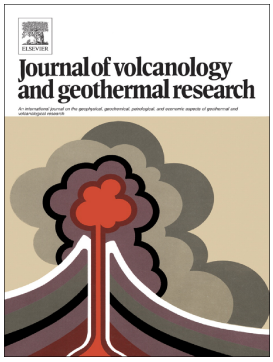

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Assessment of leachable elements in volcanic ashfall: a review and evaluation of a standardized protocol for ash hazard characterization

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Abstract

Volcanic ash presents a widespread and common hazard during and after eruptions. Complex interactions between solid ash surfaces and volcanic gases lead to the formation of soluble salts that may be mobilized in aqueous environments. A variety of stakeholders may be concerned about the effects of ash on human and animal health, drinking water supplies, crops, soils and surface runoff. As part of the immediate emergency response, rapid dissemination of information regarding potentially hazardous concentrations of soluble species is critical. However, substantial variability in the methods used to characterize leachable elements makes it challenging to compare datasets and eruption impacts. To address these challenges, the International Volcanic Health Hazard Network (www.ivhhn.org) organized a two-day workshop to define appropriate methods for hazard assessment. The outcome of this workshop was a 'consensus protocol' for analysis of volcanic ash samples for rapid assessment of hazards from leachable elements, which was subsequently ratified by leading volcanological organizations. The purpose of this protocol is to recommend clear, standard and reliable methods applicable to a range of purposes during eruption response, such as assessing impacts on drinking-water supplies and ingestion hazards to livestock, and also applicable to research purposes. Where possible, it is intended that the methods make use of commonly available equipment and require little training. To evaluate method transferability, an interlaboratory comparison exercise was organized among six laboratories worldwide. Each laboratory received a split of pristine ash, and independently analyzed it according to the protocol for a wide range of elements. Collated results indicate good repeatability and reproducibility for most elements, thus indicating that the development of this protocol is a useful step towards providing standardized and reliable methods for ash hazard characterization. In this article, we review recent ash leachate studies, report the outcomes of the comparison exercise and present a revised and updated protocol based on the experiences and recommendations of the exercise participants. The adoption of standardized methods will improve and facilitate the comparability of results among studies and enable the ongoing development of a global database of leachate information relevant for informing volcanic health hazards assessment.

Keywords: volcanic ashfall, leachable elements, hazard assessment, standardized protocol, interlaboratory comparison

1. Introduction

Volcanic ash is produced by all explosive volcanic eruptions representing a frequent and often widespread volcanic hazard. During and following an eruption, there are often major concerns from the public, civil authorities and agricultural producers about the effects of volcanic ash on human and animal health, drinking water supplies, crops, soils and surface waters (Stewart et al., 2006; Wilson et al., 2012; Stewart et al., 2018b). Freshly erupted ash contains a range of soluble elements, which may be released at different rates upon contact with water or body fluids. This can cause both beneficial effects (such as the addition of plant growth nutrients to pastoral systems) and harmful effects (such as fluorine toxicity to livestock). There is, thus, a need for standard and reliable methods for the rapid assessment of readily soluble elements as part of the immediate emergency response.

Leaching is the primary method used to quantify species adsorbed onto the surface of ash grains. Witham et al. (2005) reviewed ash leachate studies and identified a lack of consistency in analytical methods used in previous studies. These authors, who noted that the use of different leachate analysis techniques was hindering comparisons among datasets, suggested that a common leachate methodology would be beneficial, and proposed values for the important parameters of contact time, leachant and ash:leachant ratio.

In June 2011, the International Volcanic Health Hazard Network (www.ivhhn.org) convened an expert workshop at Durham University, U.K., which drew upon the collective experience of the participants to create a 'consensus protocol', published on the IVHHN website as Stewart et al. (2013). This protocol built on the methods proposed by Witham et al. (2005), and extended them to a set of recommended practices for sample collection, storage, preparation and leaching, so as to promote acquisition of high-quality leachate compositions that may readily be compared. A further goal was to enable the ongoing development of a global database of leachate information relevant for informing volcanic health hazard assessment. The protocol was subsequently ratified in early 2013 by leading volcanological organizations: IAVCEI, the Cities and Volcanoes Commission, GNS Science and the U.S. Geological Survey.

However, a review of the recent (post-2005) ash leachate literature, carried out as part of the current study (Section 2.2), has shown that there has been little progress towards the adoption of standardized methods either from Witham et al. (2005) or Stewart et al. (2013). The lack of standardized methods can be a particular problem for agencies involved in eruption response as they may be unaware of suitable and reliable methods, or appropriate

parameters to determine (Table 1). As an example, the June 2011 eruption of Cordón Caulle volcano, Chile, dispersed ash over ~350,000 km^2 of productive agricultural land, mainly in Argentina (Collini et al., 2012). Initial, in-country analysis of leachable elements in the fresh ash was performed using a standard method for analyzing borosilicate glass (ASTM Method C 169-92 Chemical Analysis of Soda-Lime and Borosilicate Glass Volume 15.02), which yielded a result of 0.7 mg F/kg dry weight ash (Hufner and Osuna, 2011) in a single sample collected ~100 km from the vent. This method varies substantially from the IVHHN protocol method, and appears to have greatly underestimated the hazard from water-extractable fluoride, as a later study (Stewart et al. 2016) reported water-extractable fluoride concentrations in fresh ash of 27 mg/kg and 167 mg/kg at comparable distances, although differing orientations, from the vent (with a range of 12-167 mg/kg F across the whole deposit). Of particular note is that several subsequent studies found F intoxication in wild deer and some livestock populations in the depositional area of the Cordón Caulle eruption, with ash ingestion asserted to be the source (Flueck, 2013, 2014; Flueck and Smith-Flueck, 2013a, 2013b). Stewart et al. (2016) noted that the situation "provided a useful lesson highlighting the need for accessible, reliable and appropriate guidance on ash analysis to enable a rapid assessment of ash toxicity hazard". A further lesson noted by Stewart et al. (2016) was the need for statistically representative field sampling of ash deposits (i.e., accounting for geographical, lithological and stratigraphic variability).

More broadly, the adoption of standardized methods will improve and facilitate the comparability of leachate analyses performed for other purposes, such as assessing the potential of ash leachates as proxies for plume chemistry and/or as monitoring tools for volcanic activity (e.g., Edmonds et al., 2003). Ayris et al. (2015) carried out a retrospective analysis of published leachate analyses from the 18 May 1980 eruption of Mt St Helens volcano, Washington, USA, to investigate gas-tephra interaction mechanisms. They noted that the use of differing leaching protocols rendered the majority of the data non-comparable and reiterated their support for adoption of standardized methods. They further noted that small leachate datasets can fail to capture the complexity of large ash deposits, and urged that spatially-representative sampling of the entire deposit be undertaken as far as possible.

The primary aim of this study was to evaluate the IVHHN leachate protocol by conducting an interlaboratory comparison exercise. Widespread adoption of a standardized protocol is contingent upon reproducibility of data amongst users and laboratories. Therefore, an interlaboratory comparison exercise was organized among six independent laboratories involved in volcanic ash leachate analyses in recent years. This manuscript reports the

outcomes of the exercise and provides recommendations based on the experiences of the participants. Standardised ash leaching methods should be used in association with other tests to assess ash hazards; for example, a protocol for assessing the respiratory health hazard of volcanic ash is available on the website of the IVHHN (https://www.ivhhn.org/images/pdf/ash_analysis_protocol_2010.pdf)_and incorporates the leachate methods recommended here.

In support of the primary aim, we also summarise recent (post-2005, following Witham et al. 2005) ash leachate literature, and describe the development and ratification of the IVHHN consensus leachate protocol.

2. Review of volcanic ash leachate literature since 2005

As described in the Introduction, leaching is the primary method used to quantify species adsorbed onto the surface of ash particles. In 2005, Witham et al. published a review of over 55 ash leachate studies. These authors evaluated applications of ash leachate data to plume gas geochemistry, calculation of volatile budgets and environmental impact assessment. Importantly, the authors noted that comparisons among different eruptions and volcanoes have been hampered by differences in methods among studies, and proposed a standardized methodology to facilitate such comparisons.

Since the landmark 2005 review, a further 56 (at time of writing) studies utilizing or referring to ash leachate methods have been published, both for hazard assessment and research purposes, and the call for standardization echoed (Gislason et al., 2011; Ruggieri et al., 2012). They are summarized in Table 2. We review these studies with respect to their purpose and methodologies. The review is intended as an overview of the wide range in leaching parameters used (summarized in Figure 1), and to assess the uptake of the standardized methodology proposed by Witham et al. (2005).

2.1. Purpose of ash leachate analyses

2.1.1. Assessing impacts to the environment, human health and/or agriculture

Some two-thirds of studies published since 2005 (38 of 56) are primarily concerned with assessing environmental, human health and/or agricultural impacts of the release of soluble elements from ashfall (Table 2). Eight of these studies are concerned with the fertilizing potential of volcanic ash in ocean surface water via the supply of trace nutrients such as iron (Fe), as a Fe deficiency limits phytoplankton growth in over 30% of the world's oceans (Maters et al., 2017; Achterberg et al., 2013; Olgun et al., 2013; Hoffman et al., 2012;

Censi et al., 2010; Wang et al., 2010; Jones and Gislason, 2008; Duggen et al., 2007). Just one study (Frogner et al., 2001) cited by the Witham et al. (2005) review was concerned with this topic. Interest in Fe sources to the ocean has increased in recent years, as marine primary productivity affects atmospheric CO_2 concentrations and thus contributes to global climate regulation (e.g., Duggen et al., 2010; Tremblay et al., 2015).

Several studies have demonstrated that pristine ash (freshly erupted samples that have not been rained on or deposited into water) rapidly releases Fe and other nutrients on contact with seawater, and have further demonstrated enhanced growth of common phytoplankton species in bio-incubation experiments using ash-dosed seawater (e.g., Duggen et al., 2007; Melançon et al., 2014). These observations are supported by ship-based sampling of ocean surface waters and remote sensing observations that identify marine phytoplankton blooms in response to specific ashfall deposition events (e.g., Hamme et al., 2010; Langmann et al., 2010). Hoffmann et al. (2012) noted that release of trace metals from ash into seawater may have both fertilizing and toxic effects on plankton species, and suggested that ash fallout may therefore change phytoplankton species assemblages.

A further two studies (Olsson et al., 2013; D'Addabbo et al., 2015) considered the fertilizing and toxic potential of volcanic ash deposition into freshwaters. Both studies reported that the ash leachates studied were only mildly toxic to aquatic biota. It is probable that the major consequences of ashfall for aquatic ecosystems are from physical impacts of suspended ash such as increased turbidity and habitat smothering (e.g., Lallement et al., 2016; Witt et al., 2017). Ayris and Delmelle (2012) provide a comprehensive review of physical, chemical and biological effects of ashfall on receiving environments.

Seven studies considered the consequences of ashfall for agroecosystems in Indonesia (Anda and Sarwani, 2012; Anda et al., 2015; Fiantis et al., 2010; 2011; Stewart et al., 2014), Argentina (Stewart et al., 2016) and New Zealand (Cronin et al., 2014). The studies of Indonesian volcanoes were concerned primarily with the impacts of the ashfall on soil fertility, whereas the studies of eruptions in Argentina and New Zealand were particularly concerned with characterizing the fluoride hazard to grazing livestock from ash ingestion. A study by Damby et al. (2018) on ash leachate composition from the 2018 eruption of Kīlauea volcano, Hawaii, also analyzed surface water and rainwater chemistry. The purpose of this work was to aid local health, environmental and agricultural agencies in assessing ashfall hazards.

A further six studies (Bia et al., 2019; Cabré et al., 2016; Canion and Landsberger, 2013; Ruggieri et al., 2012a; 2011; 2010) considered the contribution of the release of soluble

elements from ashfalls to regional geochemical fluxes, from both modern and ancient eruptions. All of these studies report that ashfalls can be substantial sources of elements to the environment, and can contribute both macro- and micronutrients, such as Ca, Fe, S and P, and potentially toxic elements such as fluorine. Ruggieri et al. (2012a) further note that the soluble 'cargo' appears to be lower in higher-silica ash, such as the rhyolitic ashfall from the 2008 Chaitén eruption, compared to lower-silica ash. This observation was borne out by a study of fluorine surface speciation in fresh ashfall from five recent South Andean eruptions (Bia et al., 2019) where the highest rates of release of F were found for the basaltic trachyandesite (55.6% SiO_2) ash from the 2016 Copahue eruption, and, conversely, the lowest rates for the rhyolitic (72.5% SiO_2) 2008 Chaitén ashfall.

Three studies have utilized leaching methods as part of a suite of human health-relevant analyses of ash from recent eruptions (Damby et al., 2013; Horwell et al., 2013 and Le Blond et al., 2010). These toxicological profiling methods are described in the IVHHN respiratory health hazard assessment analysis protocol available at http://www.ivhhn.org. A further study (Monick et al., 2013) leached Eyjafjallajökull (2010) ash as part of an investigation into the reported association between inhalation of airborne ash and respiratory infections. A recent study by Tomašek et al. (2019) assessed the potential for in-plume interactions between SO_2 and ash to influence the respiratory toxicity of ash, using *in vitro* toxicity assessment of ash leachates.

Finally, Bosshard-Stadlin et al. (2017) noted that few volcanic ash leachate studies have been conducted on volcanoes in Africa. Oldoinyo Lengai volcano, Tanzania, has the distinction of being the world's only currently active carbonatite volcano. However, the mildly explosive to effusive activity associated with carbonatite eruptions is punctuated by more explosive eruptions that erupt mixed carbonatite-silicate ash (Bosshard-Stadlin et al., 2014). Bosshard-Stadlin et al. (2017) reported that tephra from the most recent explosive eruption had surface coatings containing highly-soluble villiaumite (NaF), and suggested that this ashfall would cause toxicity hazards in shallow, open water supplies. Other elements that were notably elevated in ash leachates were As and Mo. Rango et al. (2010a,b) note the presence of a high F geochemical anomaly, also associated with high concentrations of As, U, Mo and B, in springs and groundwaters of the Main Ethiopian Rift (MER). These authors carried out an extended-duration leaching trial of both MER rhyolites and their weathered and reworked sediments, and concluded that local sediments are the main reservoir and source of F, As, Mo, U and V (Rango et al., 2010a).

2.1.2. Ash leachate compositions as proxies for plume chemistry

Nine ash leachate studies since 2005 have a primary volcanological purpose, including evaluating the potential of ash leachates as proxies for plume chemistry and/or as monitoring tools for volcanic activity (Marumoto et al., 2017; Primulyana et al., 2017; Miyagi et al., 2013; Bagnato et al., 2011, 2013; Armienta et al., 2010), calculating volatile budgets (de Moor et al., 2005, 2010) or investigating the formation or sources of ash surface coatings (Gutierrez et al., 2016; Ayris et al., 2014).

The use of ash leachate compositions to monitor volcanic activity may be specific to individual volcanoes and not readily generalized. For instance, at Popocatépetl volcano, Mexico, which poses hazards to over 20 million people, Armienta et al. (2010) observed that increases of the proportion of F in ash leachates, relative to S and Cl, preceded the growth of new lava domes (followed by destructive explosions). These authors further noted that S/Cl ratios (high values of which in some studies have been associated with degassing of incoming magma prior to large-scale explosive activity) were, in the case of Popocatépetl, complicated by the inclusion of hydrothermally-altered material, and that the use of S isotopes was necessary to distinguish magmatic from hydrothermally-generated S.

For Stromboli volcano, Italy, Bagnato et al. (2011) analyzed ash samples collected throughout the 2004-2009 eruptive activity. These authors concluded that, while ash leachate compositions are related to volcanic activity in a 'highly complex and non-linear manner', they nevertheless reflect (with increased S/F ratios) changed degassing regimes preceding large explosive events. The same authors (Bagnato et al., 2013) also studied ash leachate compositions for the 2010 Eyjafjallajökull, Iceland, eruption, using distance at which ash samples were collected as a proxy for residence time in the plume. Major ion abundances generally increased, and molar ratios of S/F and Cl/F decreased, with increasing distance, which was argued by the authors to indicate faster processing of F in the plume. However, Delmelle et al. (2014) disputed the decrease with distance of the S/F and Cl/F ratios on the basis that the relationships shown were unduly influenced by the inclusion of the most proximal sample, and noted that the correlation disappeared when this point was removed. They further disputed the formation rates derived for sulfur and halogen-bearing salts (Bagnato et al., 2013). Bagnato et al. (2014) responded by presenting data for different phases of the eruption, divided into groups with similar surface areas, showing more rapid rates of increase of F with increasing distance compared to S or Cl. The response also noted that the high reactivity of HF_g is already well-established (e.g., Oskarsson, 1980).

2.1.3. Other purposes (methodological, reviews, retrospective analyses)

Since 2005, eight studies (Table 2) have had other purposes such as comparing methods (Stewart and Leonard, 2018a); proposing new or modified methods (Ruggieri et al., 2012b; Gislason et al., 2011; and Hageman, 2007), reviewing ash leachate studies (Ayris and Delmelle, 2012; Stewart et al., 2006), carrying out retrospective analyses of published data (Ayris et al., 2015) or including leachate data as a supplement to a study with a different purpose (Borisova et al., 2013). Most are discussed elsewhere in this article so are not revisited here.

2.2. Comparison of leachate methodologies

The composition of an ash leachate will reflect the concentration of adsorbed species, but will also be operationally defined (i.e., the results depend on the method used to obtain them). A common issue identified in the literature (Witham et al., 2005; Ayris et al., 2015), and reiterated here, is that comparability of leachate data has been hindered due to methodological differences. This has been the case even for studies of the same eruption (Ayris et al., 2015).

Considering the 52 studies in Table 2 that directly utilize leaching methods to generate data, parameters vary widely. The majority (45) of the studies used batch leaching methods only; five studies used column leaching only and two used both batch and column leaching. Batch leaching is a simple procedure that involves placing a given mass of solid sample in a closed container with a specific volume of a liquid leaching solution (leachant), with some form of agitation during the contact period to ensure complete contact between the sample and leachant. Column leaching experiments (where samples of ash are packed into columns, eluted with leachants such as deionized (DI) water, synthetic rainwater or seawater, and then fractions of eluent collected at different times) are more complex but can provide a more realistic simulation of environmental processes such as rainfall leaching of ash deposits.

Of the 47 studies that used batch leaching, the parameters of leachant used, contact time and ratio of solid to leachant (S/L ratio) varied substantially among studies and are discussed separately, below and summarised in Figure 1.

2.2.1. Leachant

Some three-quarters of batch ash leachate studies published since 2005 (34 of 47, Figure 1) have used a DI water leach to extract water-soluble compounds adsorbed onto ash surfaces, sometimes in combination with the use of other leachants. The use of DI water as a leachant is generally accepted to be widely relevant and applicable to purposes such as predicting compositional changes in roof catchment rainwater tanks and livestock water

supplies, runoff into surface waters and availability of nutrients such as sulfate for immediate uptake by crops.

Four studies have used dilute mineral acid leaches as supplements to DI water leaches to provide more realistic estimates of ash ingestion hazards, usually for livestock (Stewart et al., 2016, 2014; Cronin et al., 2014; Cangemi et al., 2017). These 'simple gastric (SG)' leaches use dilute hydrochloric acid to mimic conditions in the stomach. Gastric leach tests are regularly applied to samples of contaminated soils, mine wastes and other materials to estimate the fraction of metal toxicants that will be solubilized in acidic stomach compartments and made potentially available for uptake into the circulatory system (this is termed the 'bioaccessible fraction'). Cronin et al. (2014) noted that fluoride is usually the most important toxicant to evaluate for bioaccessibility.

A further six studies have used other leachants to supplement DI water leaches. Two studies, both by Ruggieri et al. (2010, 2011), use concentrated nitric acid leachant, to assess the maximum load of potentially toxic elements that may eventually be released to the environment. Similarly, Stewart et al. (2016) determined total recoverable metals in ash from the 2011 Cordón Caulle eruption, using a modification of U.S. Environmental Protection Agency (EPA) Method 200.8 (EPA, 1994). This method uses very aggressive conditions whereby ash is digested with 50% nitric acid and 20% hydrochloric acid at 95°C. We note that these strong acid leaches dissolve glass and mineral constituents rather than just solubilizing adsorbed surface salts.

Fiantis et al. (2010) used DI water among of a suite of other leachants to assess dissolution of unweathered ash deposits in a warm, humid tropical climate. These included the organic acids citric acid ($C_6H_8O_7$) and oxalic acid ($C_2H_2O_4$) which are produced as microbial metabolites or plant exudates and are common constituents of soil solutions and groundwater. Dissolution of primary minerals was found to be accelerated by the presence of both organic and inorganic (sulfuric and nitric) acids in leaching solutions.

D'Addabbo et al. (2015) assessed leaching of surface salts from ash from Popocatépetl and Etna volcanoes into both DI water and natural lake water, and found that the release of elements was variably lower in lake water than in DI water for F, K, Mg, Mn and especially B, owing to the interaction of leached species with species already dissolved in the lake water.

Four studies used seawater as a leachant to understand the fertilization or toxic potential in aqueous environments and latent consequences for aquatic organisms (Censi et al., 2010; Olgun et al., 2013, Hoffman et al., 2012 and Duggan et al., 2007). A further study by Jones

and Gislason (2008) used seawater in flow-through leaching experiments, and showed that most elements are released at comparable rates with varying leachants, but that the greatest initial concentrations occur with DI water leachant. Censi et al. (2010) adopted a longer-term outlook, leaching pre-washed ash samples with natural sea water to consider the comparatively slow release of elements from volcanic ash relative to the readily available surface species. Whilst this approach does not provide insight into the immediate release observed for fresh ash deposition in seawater (e.g., Duggen et al., 2007), it provides longer-term insight into ecosystem impacts and, indeed, was the approach used by Witt et al. (2016) to consider coral reef recovery following an eruption.

Only one study used synthetic rainwater (0.005 M $CaCl_2$, pH5.5; Rango et al., 2010b), intended to mimic leaching by rainfall which is naturally acidic (pH ~5.6) due to the dissolution of atmospheric CO_2 (Andrews et al., 2014). This study, however, was concerned with leaching of aged volcanic deposits and thus is not directly comparable to the immediate pulse of soluble material released from fresh (non-wetted) ashfall.

Three other studies have used leachants based on standard soil science methods (Anda et al., 2016; Anda and Sarwani, 2012 and Fiantis et al., 2011). Maters et al. (2017) used dilute sulfuric acid (pH 1) for the specific purpose of simulating conditions in the volcanic plume.

Overall, while there are benefits in using leachants such as natural seawater or surface water for greater environmental realism, we recommend that DI water leaches be included in all studies to facilitate comparability with other published data on ash leachate compositions. At present, although a handful of studies have used multiple leachants, it is not possible to quantitatively assess the impact on the incompatibility of data that results from leaching with deionized water versus synthetic rainwater, seawater or freshwater.

2.2.2. Contact time

Contact (extraction) times vary widely among studies published since 2005, ranging from five minutes (Wang et al., 2010, using USGS Field Leach Test methods as per Hageman, 2007) to two years (Fiantis et al., 2011). The most common contact time reported was one hour, although it was used in only 13 of the 47 studies. This is probably due to many of the authors of these studies being involved in the initial development of the IVHHN ash leachate protocol, which recommends a one-hour leaching time. The rationale for this recommendation is discussed further in Section 3.3.1. Apart from cases where a range of contact times was applied (e.g., Ruggieri et al., 2012b; Bia et al. 2019), only one study (Monick et al., 2013) adopted the contact time of 1.5 hours suggested in the Witham et al. (2005) review. Studies utilizing longer contact times, and/or column leaching studies, will

continue to be of interest when considering long-term impacts of the dissolution of glass or minerals of lower solubility.

2.2.3. Solid to leachant (S/L) ratio

The S/L ratio (g solid: mL leachant) used in recent ash leachate studies was also highly variable, spanning over two orders of magnitude from 1:5 to 1:1000 (Figure 1). The most commonly used ratios are 1:20 (used in six studies as the sole ratio and a further four studies in combination with a 1:100 leach) and 1:25 (used in nine studies as the sole ratio), with 1:100 and 1:10 also being frequently used. These ratios are probably adopted on the basis of previous recommendations, with ratios of 1:20 and 1:100 recommended in the 2013 IVHHN leachate protocol, and a ratio of 1:25 recommended by Witham et al. (2005). There is a tendency for research groups to entrench their methods, presumably to retain comparability in their long-term datasets (e.g., Armienta et al., 2010, 2011; Stewart et al., 2016, 2014; Cronin et al., 2014; and Ruggieri et al., 2011, 2010). Groups who wish to retain their 'legacy' parameters may wish to consider supplementing these with the use of the IVHHN-recommended parameters to facilitate inclusion into global datasets.

In summary, it is clear that, despite the recommendations of Witham et al. (2005) that standardized parameters be adopted to increase comparability among different datasets, methods used in recent, post-2005 ash leachate studies have included widely-varying parameters (Figure 1). While the majority of studies have included DI water leaches, ratios of ash to leachant and contact times have been highly variable and inconsistent across different studies.

3. Development of the IVHHN leachate protocol

3.1. Working group workshop and writing of the protocol

A two-day workshop, convened by the International Volcanic Health Hazard Network (IVHHN) and hosted at the Institute of Hazard, Risk and Resilience, Durham University, UK, was held on 14-15 June 2011, to discuss best practices for ash leachate analysis, including aspects such as sampling procedures, sample storage, subsampling, ash extraction and analytical methods, quality assurance and control measures, and reporting of results. Written submissions to the workshop were provided by experts who were unable to attend in person. The 2005 review of ash leachate studies by Witham et al. (2005), which made preliminary recommendations on standard methods for characterizing ash leachates, was used as the starting point for discussions at this workshop.

Best-practice recommendations were developed from the collective experience of the core working group, taking into account the written submissions, rather than on any attempts to carry out laboratory-based optimization of parameters. The working group later noted a study by Ruggieri et al. (2012) that endeavored to optimize leaching parameters using a laboratory-based multivariate factorial design. The evidence-based conclusions from that study were integrated into continuing working group discussions, with some conclusions being integrated directly into the protocol, such as the identification of a minimum sample mass. However, not all conclusions aligned with the experiences of working group members, particularly with respect to the important parameter of S/L ratio. The optimization in Ruggieri et al. (2012) had been based on only two different types of ash, both with low soluble-salt burdens (e.g., concentrations of dominant components S and Cl ~100 and <50 mg/kg, respectively, versus mean values from the literature of 1711 and 1189 mg/kg, respectively; Ayris and Delmelle, 2012), and the working group considered that the findings are unlikely to be appropriate for all ash types. In addition to consensus on leaching parameters, the working group considered it best practice to include recommendations for sampling, sample storage, quality assurance and control, and reporting of results, which were not addressed in Ruggieri et al. (2012).

As ash is highly variable with respect to bulk composition, particle size and morphology, and surface characteristics, the working group recognized a need for the protocol to be sufficiently flexible to be applicable to 'unknown' ash samples, and also to draw users' attention to the need for more detailed investigations beyond the outlined methods, if necessary (see Section 5.5 for discussion on re-extraction).

We also note that leaching methods may be usefully deployed in conjunction with other methods such as X-ray photoelectron spectroscopy (XPS) to directly analyze surface chemical compositions (Ayris et al., 2014; Gislason et al., 2011) or solubility modelling with PHREEQC (Bia et al., 2019; Tomasek et al., 2019).

The outcome of the workshop was a draft protocol written and reviewed by the workshop participants and external contributors. Further review was provided by staff of the U.S. Geological Survey. This document was then ratified by IAVCEI, the U.S. Geological Survey, GNS Science and the Cities on Volcanoes Commission and was available for download from the IVHHN website between June 2013 and December 2019. The draft protocol has been revised as an outcome of the current study (Section 5.1).

3.2. Rationale for protocol methods

The purpose of the IVHHN protocol is to recommend clear, standard and reliable methods for the rapid assessment of hazards from leachable elements. The protocol methods and parameters were decided through expert consensus, using the collective experience and expertise of the workshop participants with support from the literature. The general intention of this protocol is that it will be used for the rapid analysis of ash in order to provide timely information to emergency managers and agencies during and following an eruption. Where possible, methods are based on commonly available equipment and are designed to require little training to use.

Three types of leaching tests were considered during protocol development: a general-purpose water leach, a simple gastric leach to assess human and animal ingestion hazards, and a simulated lung fluid leach to assess inhalation hazards to humans.

3.2.1. Deionized water leach

Leaching with deionized (DI) water is generally accepted as reflecting the dissolution of readily water-soluble compounds adsorbed onto ash particle surfaces (Ayris et al., 2015). It is important to note that the release of elements into natural waters may differ from their release into DI water, but after considering the merits of a range of alternative leaching solutions, the working group concluded that DI water is the most appropriate solvent due to its wide availability and standard properties. This 'general purpose' water leach is applicable to situations such as predicting compositional changes in roof-fed rainwater tanks (Cronin et al., 2014) and livestock watering troughs (Wilson et al., 2009; Stewart et al., 2016; Bosshard-Stadlin et al., 2017), runoff into surface waters (Stewart et al., 2016) and nutrient or toxin availability for immediate uptake by crops (Cronin et al., 1998). It is also the most appropriate basis for comparison among different datasets, or to global maximum, mean, median and minimum values for ash leachate compositions determined from all published leachate data by Ayris and Delmelle (2012).

The rationale for recommending two complementary S/L ratios of 1:20 and 1:100 was that, at the higher S/L ratio (1:20), the leachate solution may reach saturation with poorly-soluble mineral phases such as gypsum ($CaSO_4$), which would lead to, in this instance, an underestimate of the readily-soluble calcium and sulfate on the non-wetted ash. At the lower 1:100 ratio, problems with detection limits may be encountered for minor elements. The use of two ratios also provides an internal comparison. These specific ratios were also chosen because they are used in other, closely-related standard methods such as USEPA Method 1312 which simulates rainfall leaching (USEPA 1994) and the U.S. Geological Survey's

Field Leach Test (Hageman 2007) which both use a 1:20 S/L ratio, and the SBRC method for bioaccessibility (see Section 3.3.2) which uses a 1:100 S/L ratio.

While rates of release of elements from ash may differ for different ash samples, there is mounting evidence from both column leaching studies (Jones and Gíslason, 2008) and batch extractions with varying contact times (D'Addabbo et al., 2015; Gíslason et al., 2011; Censi et al., 2010; Fiantis et al., 2010; Duggen et al., 2007) that most elements are rapidly released, thus supporting the use of short contact times. These studies are relatively consistent: D'Addabbo et al. (2015) report that most adsorbed elements are released within an hour; Jones and Gíslason (2008) report that 90% of adsorbed elements are released within an hour, and Bagnato et al. (2013) reported that >90% of adsorbed compounds were released within two hours. Release rates within the first 10-15 minutes are likely to be highest (Olsson et al., 2013; Duggen et al., 2007).

The workshop participants recommended a contact time of one hour, as a practical trade-off between sufficient time for release of readily-soluble elements versus the time-sensitive nature of response to volcanic crises and demands for information (Stewart et al., 2018b). Very short contact times would likely be unworkable because subsequent steps such as filtration create processing bottlenecks which could, in turn, lead to inconsistent contact times. Longer contact times (e.g., four or 16 hours) have proved to be unnecessary in studies where a range of contact times were applied, returning equivalent data to shorter duration leaches (e.g., Ruggieri et al., 2012b). Similarly, Hageman (2007) noted that mine waste samples analyzed by both the USGS Field Leach Test (which has a five-minute contact time) and USEPA Method 1312 (18±2 hour contact time) returned similar water-soluble concentrations of several major ions and trace metals.

3.2.2. Simple gastric leach

Children may deliberately or accidentally ingest ash that adheres to their hands. In general, adults are unlikely to ingest significant quantities of ash, although in heavy ash environments, both adults and children may accidentally ingest substantial quantities of inhaled ash particles that are cleared from the respiratory tract. Livestock can ingest substantial quantities of ash along with their food, with close-grazing animals such as sheep being particularly susceptible. This process has led to cases of livestock poisoning and death with even thin ashfall deposits (Cronin et al., 2003; Flueck et al., 2016 and references therein).

Gastric leach tests are regularly applied to samples of contaminated soils, mine wastes and other materials to estimate the fraction of metal toxicants that will be solubilized in acidic

stomach compartments and become available for uptake in the small intestine (e.g., Wolf et al., 2008; Plumlee et al., 2013). This is termed the bioaccessible fraction, and is usually expressed as the percentage of the total recoverable amount of a particular toxicant. Although the term 'bioaccessible' is sometimes used interchangeably with 'bioavailable', the latter term refers to the fraction of an administered dose of a toxicant that is absorbed via an exposure route, reaches the bloodstream and is transported to a site of toxicological action.

Although the amounts of metals present in most volcanic ash samples are typically well below levels that can be found in mine wastes or contaminated soils, the results of a gastric leach test applied to ash samples may provide insights into potential metal uptake pathways for various ash-exposed species with acid stomach compartments following ingestion.

Bioaccessibility test methods range from simple to complex. At the complex end, methods such as the UBM (Unified BARGE Method developed by the Bioaccessibility Research Group of Europe, BARGE 2010) involve the preparation of four different simulated digestive fluids comprised of inorganic salts, organic compounds and enzymes, followed by a 20-step extraction procedure. At the simple end, a method developed by the Solubility/Bioavailability Research Consortium (SBRC) involves shaking the sample for one hour in a solution of 0.4 M glycine acidified to pH1.5 with HCl. Advantages of the UBM are that it is physiologically-based, and good *in vitro*/*in vivo* correlations (for the metals Cd, Pb, Sb and As in soils) have been obtained (Denys et al., 2012). Disadvantages are that the method is complex, time-consuming, and subject to between-laboratory variability (Wragg et al., 2011). Golder Associates (2016) evaluated both the UBM and the SBRC methods against a wide range of criteria relating to appropriateness for regulatory use for contaminated land and concluded that the SBRC method is preferable. They further noted that the SBRC method has EPA approval for assessing lead in soils (USEPA, 2009).

For volcanic ash, fluoride is generally the most important toxicant to evaluate for gastric bioaccessibility (Armienta et al., 2011). Following the 1995-1996 Ruapehu, New Zealand eruptions, DI water extractions of ash did not indicate excessive quantities of water-soluble fluoride yet several thousand sheep died from fluorosis following the eruptions (Cronin et al., 2003). These authors concluded that the phreatomagmatic nature of some of the eruptions led to the formation of calcium and aluminum fluoride and phosphate adsorbed phases which are sparingly soluble in water but may be much more soluble in the digestive system of grazing animals. For the 2012 eruption of Tongariro volcano, New Zealand, Cronin et al. (2014) reported that two to three times more fluoride in ash from the 2012 eruption of

Tongariro volcano was extracted by a simple gastric leach (a leach that simulates the conditions of the stomach) compared to a water leach, and recommended the use of simple gastric leaches for a more realistic assessment of hazards of ash ingestion to grazing animals.

For the IVHHN leachate protocol, the working group concluded that a simple test method that could be consistently used by different laboratories would be most appropriate for eruption response situations. The 'simple gastric leach' is streamlined further from the SBRC method and involves extracting the sample with 0.032 M HCl (pH 1.5). Parameters of a one-hour contact time and S/L ratio of 1:100 are adopted from the SBRC method. Size fractions of <2 mm (for animal ingestion) and <250 μm (for human ingestion) are recommended because animals are thought to ingest the whole ash sample along with food whereas children are more likely to ingest finer size fractions adhering to their hands. Extraction at room temperature (typically 20 ºC for a laboratory) is recommended rather than the physiologically-relevant temperature of 37 ºC recommended by the SBRC method, on the grounds that typical volcano observatories would be unlikely to have the necessary equipment for this step. No leachate studies have been published at both 20 ºC and 37 ºC using volcanic ash to date (Table 2).

The working group acknowledged that the proposed method to assess bioaccessibility may not closely mimic human or animal ingestion and digestion processes but, rather, is a simple, rapid method intended to provide insight into the additional solubility of toxicants under acid conditions in the digestive system.

3.2.3. Simulated lung fluid leach

Simulated lung fluid (SLF) mimics the composition of the human lung lining fluid, which is the first physical interface with which inhaled materials come into contact in the airways. It is used in leachate studies to assess the *in vitro* bioaccessibility of a wide range of respirable materials (Plumlee and Morman, 2011 and references therein). There are varying formulations for SLF but, generally, it is a near-neutral (pH 7.4) solution that contains a mixture of electrolytes and organic constituents (Gamble, 1967, Moss, 1979). The solution consists of a balance of cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) and anions (HCO_3^-, Cl^-, HPO_4^{2-}, SO_4^{2-}), at concentrations representative of those measured in lung lining fluid, often with acetate ($H_3C_2O_2^-$) or citrate ($H_5C_6O_7^{3-}$) substituting for macromolecules such as proteins and lipids (Colombo et al., 2008; Midander et al., 2007; Stopford et al., 2003). Bioaccessibility relevant to pulmonary health can also be investigated using an artificial lysosomal fluid (ALF), which mimics the intracellular environment that particles encounter following phagocytosis (cell

uptake) by alveolar macrophages. ALF comprises a similar mix of physiologically-relevant constituents, but is more acidic (pH 4.5).

At the 2011 workshop, the working group proposed inclusion of a method for SLF leaching in the protocol, intended to assess the potential respiratory hazards posed by leaching of toxicants from respirable ash. The recommendation was the use of a modified Gamble's solution as the leachant (from Caboche et al., 2011, and adapted from Davies and Feddah, 2003), which includes a realistic suite of electrolytes yet is relatively simple with respect to organic constituents, together with a physiologically-relevant size fraction of < 38 µm (the smallest available mechanical sieve at the time), a contact time of 24 hours and a 1:100 S/L ratio (Stewart et al., 2013). The group noted, however, that omission of key organic compounds could potentially under- or overestimate the true bioaccessibility for potentially toxic elements.

To date, the impact of various SLF modifications on bioaccessibility for volcanic ash is poorly constrained, and testing the viability of SLF and ALF for use in the assessment of hazards from trace elements present in volcanic ash is part of ongoing work by (some of) the authors. Efforts to develop and implement an SLF protocol have faced two primary complications. First, there is no general consensus in the wider leaching community on the physiological relevance of the various assay parameters (fluid composition, extraction time, S/L ratio, temperature, agitation) and their relevance for the inhalation pathway (see review by Kastury et al. 2017). The lack of a standardized approach and of *in vitro/in vivo* correlations thus hinders the comparisons among the studies and limits the predictive power of methods used, respectively. The second reason is technical: measuring concentrations of elements that are commonly abundant in ash leachates (e.g., Ca, Na, Mg, Cl, S) in a SLF leach is not straightforward due to matrix effects (i.e., measurement interference caused by dissolved ions (matrix constituents) in the solution). Since these ions are already present in the SLF in high concentrations (i.e., high background values) as either components of the recipe or as impurities in the reagents used to prepare the SLF, this can cause a signal reduction or poor precision during measurement, thus causing difficulties in determining concentrations leached from the ash. Making large dilutions is necessary, thereby limiting analysis of minor elements of interest as potential toxicants (e.g., Cu, Cr, Ni, Pb and Zn).

Therefore, until further evaluation has been conducted, the IVHHN leachate protocol does not include a method for SLF leaching.

4. Evaluation of IVHHN leachate protocol using an interlaboratory comparison exercise

The working group considered that the next step in the development of this protocol as a fit-for-purpose and authoritative resource would be to evaluate the methods using an inter-laboratory comparison of a bulk ash sample. This allows for repeatability and reproducibility to be assessed and, therefore, transferability of the protocol for use in other laboratories. The primary focus of this exercise was the DI water leach, but most laboratories also provided data for the gastric leach. The synthetic lung fluid leach was not included due to its complexity and unresolved technical difficulties (see Section 3.3.3).

4.1. Interlaboratory comparison exercise

An international, interlaboratory comparison was set up to determine data reproducibility across six independent laboratories. The design of the study was agreed upon by all participants. A pristine (non-wetted) bulk ash sample was split into subsamples and shipped to the participating laboratories. Each laboratory was instructed to perform a leachate analysis with three independent replicates on the sample received, following the methods described in the IVHHN leachate protocol (Stewart et al., 2013). The participants were provided with a standardized reporting form but otherwise given no additional advice or information and were asked to use their normal equipment and techniques (Table 3). As per the protocol, participants were asked to test for a broad range of elements, including plant growth nutrients, potentially toxic elements and other elements of interest for geochemical cycling. The participating institutions were: Durham University, UK; GNS Science, New Zealand; Massey University, New Zealand; Universidad Nacional Autónoma de México, México; UCLouvain, Belgium; and the U.S. Geological Survey, USA. Each laboratory was assigned a random laboratory code for reporting purposes.

4.2. Ash sample for analysis

A ~0.6 kg bulk sample of pristine ash from the 13-15 February 2014 VEI 4 eruption of Kelud volcano, Java, Indonesia, was collected from a flat concrete surface in the city of Yogyakarta, Indonesia (300 km from source) on 15 February 2014. It was shipped to Durham University, U.K. Once received, the sample was homogenized by gently rotating it in its bag and then divided into subsamples by manual coning and quartering, a method which Horwell (2007) showed was adequate for representative sampling of ash. Subsamples of either 50 g or

80 g (depending on the range of analyses to be attempted) were then shipped to the six participating laboratories around the world. Participants were not informed of the origin of the ash sample beforehand.

The reliability of the assessment and the performance of each laboratory is dependent upon the stability and homogeneity of the sample used. Though volcanic ash is inherently inhomogeneous, we assume that the sample mixing and splitting methods and the mass of material used per analysis are sufficient to overcome heterogeneities in the sample (see Figure 3 in Horwell, 2007). The variability associated with sample inhomogeneity is likely to be approximately 2% (IAEA, 2016) although we note that the preparation of certified reference materials by the International Atomic Energy Agency (IAEA) involves a more extensive homogenization procedure than was the case in our study.

4.3. Extraction and measurement equipment

All laboratories used existing in-house equipment for extraction and analysis of leachates. No two laboratories used identical materials and extraction equipment (Table 3). Anion concentrations were predominantly determined by ion chromatography (IC), with some laboratories opting for use of ion selective electrodes (ISE) or other methods such as colorimetry (Table 4). Cations were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), flame, graphite furnace or hydride generation atomic absorption spectroscopy (AAS) and ultraviolet–visible spectroscopy (UV-Vis) (Table 4).

4.4. Data evaluation

The aim of this exercise was to determine the 'reproducibility' of the test method. That is, the degree of agreement among results from experiments carried out by different individuals, at different laboratories, with different equipment and consumables, and where only the sample and test parameters are assumed to be identical. This serves to verify that the protocol can be successfully reproduced in its entirety and produces comparable data. Given the small size of the dataset (six participating laboratories), a non-parametric modified Z-score approach was used for statistical analysis. The modified Z-score approach measures how much a particular value differs from the median value of all measurements (Iglewicz and Hoaglin, 1993) and is routinely used for proficiency testing of laboratory performance (e.g., IAEA, 2016). Scores of $|z| < 3.5$ were considered satisfactory, whereas $|z| \geq 3.5$ were considered statistically different to the other measurements in the dataset (outliers). Only

datasets with at least four reported results were subjected to statistical analysis. For datasets containing no outliers, there are no statistical differences among laboratories. For outliers identified within datasets, these laboratories are described as 'under-reporting' or 'over-reporting' relative to the other laboratories as appropriate. Reproducibility was further assessed by considering relative standard deviations (RSDs) among laboratories.

'Repeatability', or the variation in measurements taken within each single laboratory, was assessed by use of RSDs, calculated for triplicate measurements of each analyte. It was not the role of the organizers to troubleshoot issues of repeatability for individual labs. The competency of each laboratory, in both preparing the test sample correctly and analyzing the leachate, is considered as a potential source of error.

T-tests (one-tailed, two-sample equal variance) were used to evaluate differences between 1:20 and 1:100 extractions, for each analyte where at least four results were reported.

4.5. Interlaboratory comparison exercise results

All six laboratories returned data for DI water and five for simple gastric leaches. Summary figures for major cations, minor cations and anions, at ratios of both 1:20 and 1:100, are shown in Figures 2a-4b, with all data available as Supplementary Material 1 (SM1). Figure 5 shows summary data for the gastric leach, at the ratio of 1:100 only.

4.5.1. Repeatability for deionized water leach

For pH and conductivity, repeatability was very high for all laboratories with a typical RSD of 1-2%. For major cations (defined here as concentrations >10 mg/kg) and anions, repeatability was also very high (RSD <2-3%) in most cases although, for 1:100 potassium, Lab A had a RSD of 51% as a result of one elevated repeat. For minor elements (<10 mg/kg), RSDs were generally higher, approaching or exceeding 100% in some cases, probably as a consequence of concentrations being close to detection limits. However, this was not the case for all minor elements; for instance, for strontium, eight of the nine mean values reported have RSDs of 3% or better.

4.5.2. Repeatability for simple gastric leach

For most laboratories, repeatability for the SG leach was <10% for most elements. For several trace elements, repeatability is better for the SG leach than the corresponding DI leach. For instance, RSDs for the 1:100 DI water leach for aluminum range from 5-61%, but for the SG leach are much lower at 1-3%. This is likely because the SG leach extracted over

300 times more aluminum from ash than the DI leach (Table 6), so concentrations measured are much greater than detection limits.

4.5.3. Reproducibility for deionized leach

For the DI leach, there are no statistical differences among groups in measured pH and conductivity of the leachate solutions (i.e., no measurements were outliers). For pH, measurements ranged from 5.2 to 5.9 (1:20) and from 4.8 to 6.1 (1:100). Specific conductance ranged from 135 to 244 μS/cm at 1:20, with Lab B under-reporting, and 38 to 56 μS/cm at 1:100, with Lab A and Lab D both under-reporting.

For major anions, Lab B under-reported chloride, sulfate and fluoride compared to the other laboratories at 1:20 (Figure 2a); whereas, at 1:100, Lab A over-reported sulfate and Lab C over-reported chloride (Figure 2b). Between-laboratory RSDs ranged from 6% for sulfate at 1:100, to 31% for fluoride at 1:20. The RSD for 1:20 fluoride reduced from 31% to 5% if the data for Lab B were omitted; RSDs for chloride and sulfate also reduced if Lab B data were omitted.

Three of the six laboratories did not attempt to measure bromide or phosphate. Two labs were unable to detect bromide, but one lab reported bromide in the range 5-10 mg/kg ash. Phosphate was <1 mg/kg. Nitrate values were highly variable among labs, with lab C reporting extreme outliers (values that were four to five orders of magnitude higher than those determined by the other laboratories) at both 1:20 and 1:100.

For major cations, Lab B reported lower concentrations for calcium, magnesium, sodium, manganese and potassium than the other labs at 1:20 (apparent in Figure 3), although only calcium, manganese and sodium were outliers. At 1:100, Lab D over-reported potassium, and Lab C over-reported manganese. Between-laboratory RSDs ranged from 5% (Ca, 1:100) to 19% (Mg, 1:100). As was the case for anions, 1:20 RSDs reduced in all cases if Lab B data were omitted.

For minor elements, few outliers were identified for aluminum, barium, boron, cobalt, copper, lithium, nickel, strontium or zinc (elements with at least four labs reporting) at either ratio. Lab F under-reported lithium at 1:20 and over-reported zinc at 1:100. Labs C and F over-reported barium at 1:100. Between-laboratory RSDs were generally higher than for major elements and ranged from 5% for cobalt at 1:100 to 142% for nickel at 1:100. There were insufficient data to assess reproducibility for arsenic, cadmium, chromium, iron, lead, silicon, selenium and titanium.

4.5.4. Reproducibility for simple gastric leach

For the SG leach, samples were only analyzed at 1:100. No laboratory reported data that were systematically different from other laboratories across several elements (Figure 5). Only a few outliers were of note: Lab B over-reported aluminum; Lab E over-reported arsenic, though mean values ranged from 0.20-0.26 mg/kg across all reporting laboratories; and Lab D over-reported manganese. None of these elements was of note for the corresponding laboratories for the 1:20 or 1:100 DI water leach.

4.5.5. Comparison of 1:20 and 1:100 deionized water leaches

Considering mean concentrations across all labs, 1:20 leaches returned lower concentrations than 1:100 leaches for all 16 elements for which four or more labs reported results at both ratios (Table 5). While this trend was systematic, differences between these means were only statistically significant ($p<0.05$ using t-testing) for magnesium ($p=0.03$) and copper ($p=0.002$). Some of these differences are due to the lower results reported by Lab B for the 1:20 leach (evident from Figures 1, 3 and 5) as the difference between the two ratios reduces when Lab B data are removed.

4.5.6. Comparison of 1:100 deionized water and simple gastric leaches

For a range of potentially toxic elements, the simple gastric (SG) leach extracted greater quantities of elements than the DI water leach, at the 1:100 ratio (Table 6). The SG/DI ratio was highest for the elements iron and aluminum (>300, although we note that there is a high degree of uncertainty in these ratios because of the poor reproducibility for the DI water extractions), and lowest for nickel and zinc.

5. Discussion

5.1. Revision of original IVHHN consensus leachate protocol

Based on feedback from users and the experiences of the leachate working group since 2013, the original protocol has been revised. No changes were made to the recommended leaching parameters. We streamlined the content in order to increase the focus on the laboratory procedure, and made the following key changes:

- Addition of a table of contents to allow for quick referencing;
- Background material was removed and has been covered in greater detail in this article;
- Sample collection advice was strengthened to reinforce the need for representative sampling of an entire ashfall deposit (after Ayris et al., 2015);

- Removal of the SLF leach due to 1) the current lack of expert consensus on appropriate methods, and 2) the complexity of the method making it unsuitable for use as a response tool;
- Removal of USGS field leach test as this is already available as a standalone method (Hageman, 2007);
- Retitling of 'gastric leach' as 'simple gastric leach' to reflect the fact that the method adopted is a simpler version of standard gastric leach methods;
- Addition of a section on how to carry out re-extractions, which has proved valuable in assessing hazard more realistically in specific situations (Cronin et al., 2003, 2014).

The revised protocol is included as SM2 and can be downloaded from the IVHHN website at the following link: https://www.ivhhn.org/images/pdf/volcanic_ash_leachate_protocols.pdf

5.2. Discussion of results

Repeatability, or the variation in measurements taken within each single laboratory, was generally very high (<2-3%) for the parameters of pH, conductivity and major cations and anions. This implies that the homogeneity of the ash sample is similar to that of the certified reference material IAEA-457 (IAEA, 2016). For minor elements, repeatability was lower, likely as a consequence of measured concentrations being close to detection limits. Of the 36 datasets that were analyzed (18 parameters per ratio with sufficient data reporting), 17 contained outliers. Some of the outliers were systematic, such as under-reporting by Lab B at 1:20, whereas others were apparently random.

Reproducibility was further assessed using between-laboratory RSDs. Various approaches to establishing thresholds for reproducibility in inter-laboratory comparison exercises have been used. For example, Wragg et al. (2011) carried out an inter-laboratory comparison for the unified BARGE method for assessing bioaccessibility, for copper, lead and arsenic in soils, and proposed a 'pass mark' of ≤20% as the benchmark criterion for between-lab RSDs. Of the datasets assessed by Wragg et al (2011), three out of eight (37.5%) passed the benchmark criterion. Applying a similar approach to our datasets, 22 of the 36 datasets analyzed (61%) have RSDs ≤20% and thus pass the benchmark criterion. If the systematically-low results for Lab B are excluded, the proportion of datasets passing the benchmark criterion rises to 69%.

As described previously, the rationale for recommending two ratios of 1:20 and 1:100 in the IVHHN protocol was that, at the higher S/L ratio (1:20), the leachate solution may reach saturation with poorly-soluble mineral phases, while problems with detection limits

may be encountered at the lower S/L ratio (1:100). While 1:20 extractions systematically returned lower concentrations of elements than 1:100 extractions (Table 5), the differences were only statistically significant for two of the 16 elements analyzed. It is important to note here that just one ash sample was analyzed in this exercise, and this ash sample, from Kelud volcano, Indonesia (an andesitic arc volcano) has a low overall burden of soluble salts compared to a global dataset on water-extractable elements in volcanic ash compiled by Ayris and Delmelle (2012). Therefore, saturation effects may be more pronounced for ashes with higher soluble salt burdens.

The simple gastric leach is intended to provide insight into the additional solubility of toxicants under acid conditions in the digestive system. The elements iron and aluminum showed the greatest enhancement (SG/DI ratios >300) of solubility under acid conditions (Table 6). This finding was also reported for 2014 Sinabung ash (Stewart et al., 2014), and 2012 Tongariro ash (Cronin et al., 2014), although SG/DI ratios were lower (13-70 for Al and 19-93 for Fe). For the toxicologically significant element F, similar SG/DI ratios are reported by the current study (2.4), Cronin et al. (2014) (2.2-2.8) and Stewart et al. (2014) (3.8). However, for the 2011 Cordón Caulle rhyolitic eruption, simple gastric leaches did not systematically extract more fluoride than water leaches (Stewart et al., 2016). This was interpreted to imply that F was present on the ash in readily-soluble forms. These data support the suitability of a separate gastric leach, in addition to a DI leach, to provide additional information about element availability.

5.3. Influence of instrumental techniques on results

The six laboratories utilized a range of instrumental techniques to analyze leachate solutions for major and minor cations and anions (Table 4). Because of the small size of the dataset, it is not possible to apply statistical comparisons between different methods for each parameter measured. The high detection limits associated with AAS limited the ability of Lab D to report on concentrations of most minor cations in deionized water leaches.

For anions, no outliers are associated with the use of different techniques (i.e., IC or ISE for Cl and F determination, and IC and turbidimetry for SO_4 determination). Determination of F by ISE is relatively inexpensive and fast, which may be key advantages in an eruption response. However, ISE is more suited to experienced analysts as the method is subject to analytical interferences which may be overcome by adding appropriate reagents to the solution, but which may require some knowledge of the sample composition.

5.4. Pitfalls and errors identified

The interlaboratory comparison was useful for verifying operational details of the protocol but also for identifying issues at particular laboratories. Lab B systematically reported lower concentrations than other laboratories for the 1:20 extraction (Figures 2a, 3a and 4a; Table 5) although this was only statistically identifiable for SO_4, Cl, F, Ca, Na and Mn. Troubleshooting with the laboratory personnel, after data were submitted to the organizers, identified inadequate mixing of the ash sample and leachant as the likely cause, as a relatively gentle orbital motion shaker was used. We note that the use of rotary or end-over-end shakers is preferable to promote complete mixing, and have modified the equipment list in the protocol accordingly.

Lab A had problems with blank contamination for some elements. Here the analyses were performed in a general soil sciences laboratory where some use of shared equipment was unavoidable. This reinforces the importance of including procedural blanks, preferably run in triplicate, in the IVHHN leachate protocol.

Lab D noted that it took approximately five minutes for the fluoride ion-selective electrode to stabilize after the electrode was immersed in the leachate solution with TISAB buffer added.

5.5. Value of expert judgement

Investigations beyond the protocol methods may be worthwhile for some ash samples (as suggested in Section 4.1). As an example, single one-hour leaches may, in some circumstances, underestimate the environmental availability of agriculturally important elements, such as fluorine and sulfur (Cronin et al., 1998; Cronin et al., 2003; Cronin et al., 2014). For fluorine, this is particularly the case for ash generated by phreatomagmatic eruptions through vent-hosted hydrothermal systems, where F may be present as slowly-soluble compounds such as CaF_2 or AlF_3 (Cronin et al., 2003). A further example is the analysis of ash with highly-unusual composition, such as ash from the carbonatitic Oldoinyo Lengai volcano, Tanzania (Bosshard-Stadlin et al., 2017) where concentrations of leachable sodium, potassium, lithium, chloride and molybdenum far exceeded previously-published ranges (Ayris and Delmelle, 2012). In these situations, users are advised to carry out sequential leaches (re-extractions) to provide a more complete assessment of the potential of the ash to release potentially toxic elements to the environment; for example, if there is repeated rainfall onto ash deposits.

Re-extractions may also be important for sulfur, as very high concentrations of sulfate-S (sulfur (S) in the form of sulfate) may lead to mineral saturation (e.g., gypsum) occurring in

a single leach, particularly at the 1:20 ratio. This was the case in Damby et al. (2018) for ash from the 2018 eruption of Kīlauea. Comparison of their 1:20 and 1:100 data indicated that their 1:20 leachates were likely sulfur-saturated, and, given the tremendous sulfur emissions during the eruption and the propensity for ash to act as a sulfur sink (e.g., Ayris et al., 2013) as well as an abundance of plume-derived gypsum and anhydrite in the samples, it was determined that their 1:100 leachate data more appropriately captured the hazard. Re-extractions to deal with the high concentrations of sulfate-S together with solubility modelling could be used to confirm their conclusion.

In some cases, values for certain elements may be higher than expected. Values that are substantially higher than previously published ranges could result from contamination. Reference to previously published ranges and averages (see Ayris and Delmelle, 2012) can be worthwhile in such situations. Cronin et al. (2014) recorded a very high zinc concentration (437 mg/kg) in water leachates of ash from the 2012 Te Maari eruption, collected from a galvanized metal roadside barrier, and concluded that inadvertent contamination of the sample was the most likely explanation as all other samples had water leachate zinc concentrations of approximately 5 mg/kg or less. In the same study, a high copper concentration (52 mg/kg) was recorded in a sample collected from a wooden fence post. Concentrations of arsenic and chromium were also elevated in this sample, suggesting contamination by CCA (copper-chrome-arsenate) timber preservative. These examples serve to reinforce the advice in the IVHHN leachate protocol to always record the surface each sample is collected from and, if possible, to leave a small margin between the bottom of the sample and the surface to minimize the chance of contamination from the collection surface. In the present dataset, nitrate values reported by Lab C were far higher than would be expected for volcanic ash. Given that these values were strong outliers, it is possible that they represent contamination at some point during the leaching procedure.

Our review of published leachate data indicates that leachable concentrations are low or below detection for elements where speciation is a primary concern for toxicity (in particular, As, Cd, Cr, Se and Hg). However, in instances where there may be specific concern, methods other than this leachate protocol would be required to investigate fully.

6. Conclusions

Consistency in data collection is the foundation for linking leachate datasets with empirical eruption impacts, and it provides the framework for translating lab-derived fragility functions into eruption response efforts. Implementation of standardized methods is essential

for ensuring reproducibility and comparability amongst laboratories. We have developed and tested a leachate protocol for use to such ends. A comparative review of post-2005 studies and methods has encouraged further discussion and since bolstered the conclusions of a draft leachate protocol produced in 2013. The leachate protocol overcomes the common causes of incomparability amongst datasets reported in the literature, such as leachant used, S/L ratio, and contact time. However, it is essential that appropriate spatial and temporal sampling still be undertaken where possible. Experience has shown that single-sample and/or post-eruption analyses are insufficient or too late; that is, rapid but not reliable, or reliable but not rapid. Wherever possible, the protocol makes use of commonly available equipment in order to achieve continuous, near real-time data collection during a crisis. This is intended to enable immediate, low-cost in-country analysis in order to facilitate time-sensitive input into the emergency response.

Our interlaboratory comparison exercise returned comparable data amongst participating laboratories, indicating good reproducibility and transferability of the protocol. Little instruction is needed for reliable results from laboratories experienced in these types of analyses. We suggest that laboratories interested in conducting leachate analyses coordinate with capable laboratories for proficiency testing. We also suggest that coordination of laboratories that have the capabilities to conduct leachate analyses with laboratories that do not have this ability benefits the greater volcanology community through hazards assessment and contribution of robust data to a growing dataset.

7. Abbreviations

AAS	Atomic absorption spectroscopy
BARGE	Bioaccessibility Research Group of Europe
BGS	British Geological Survey
CRM	Certified reference material(s)
DI	Deionized water
EPA	Environmental Protection Agency
GF-AAS	Graphite furnace atomic absorption spectroscopy
HDPE	High density polyethylene
HG-AAS	Hydride generation atomic absorption spectroscopy
IAEA	International Atomic Energy Agency
IC	Ion chromatography
ICP-MS	Inductively coupled plasma mass spectrometry

ICP-OES	Inductively coupled plasma optical emission spectrometry
IFR	Institute of Food Research, U.K.
ISE	Ion selective electrode
IVHHN	International Volcanic Health Hazard Network
MER	Main Ethiopian Rift
RSD	Relative standard deviation
SBRC	Solubility/Bioavailability Research Consortium
SG	Simple gastric
TISAB	Total ionic strength adjustment buffer (used in ISE determinations)
UBM	Unified BARGE method
USGS	United States Geological Survey
UV-Vis	Ultraviolet–visible spectroscopy
VEI	Volcanic Explosivity Index

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List of tables, figures and supplementary material

Table 1 Typical ash leachate parameters of interest for different purposes[1]

Purpose	**Parameters of interest**	**Examples**[2]
Assessing health hazards of ash to humans and livestock (via ingestion or inhalation pathways)	pH, As, Cd, Cu, Cr, **F,** Fe, Ni, Pb, **SO_4,** Zn	Cronin et al. 2014 Damby et al. 2013 Horwell et al. 2013
Assessing potential of ash to contaminate drinking-water supplies	pH, **Al,** As, Cd, Cr, Cu, **F, Fe, Mn,** Ni, Pb, **Zn**	Stewart et al., 2006 Cronin et al. 2014
Inferring plume chemistry	pH, **Cl, F, SO_4**	Armienta et al. 2010 Miyagi et a. 2013 Primulyana et al. 2017
Assessing potential of ash to contribute nutrients to soil	**pH,** B, **Ca,** Co, Cu, **K, Mg, Na,** Se, NO_3, PO_4, **SO_4**, Zn	Cronin et al. 1998 Anda et al. 2016 Stewart et al. 2016

[1] The authors emphasize that these suites of parameters are suggestions rather than an exhaustive list. Bolded parameters are likely of greatest significance.

[2] Refer to Table 2 for additional examples from the literature

Table 2 Review of ash leachate studies published since 2005 categorised by primary purpose of study

Study	Volcano/es	Summary	Batch leaching details			Column leaching details		Further details on methods
			Contact time	Ratio (g ash:mL leachant)	Leachant	Leaching rate	Leachant	
Primary purpose of study: assessing health, agricultural and/or environmental impacts of ashfall								
Bia et al., 2019	Hudson, Chaitén, Puyehue, Calbuco, Copahue	To identify F-bearing phases and assess release rates into aqueous reservoirs	1.5, 24, 72, 168, 240 and 336 h	1:20	DI adjusted to pH 3.0, 6.5 and 10.0 with HNO_3 or NaOH			Extractions conducted at pH 3.0, 6.5 and 10.0. Batch leaching protocol followed Armienta et al. (2002) and Witham et al. (2005). Samples were re-extracted at each of the contact times specified by completely withdrawing the supernatant and adding further extractant.
Tomašek et al., 2019	Not applicable	To investigate whether in-plume interactions of ash particles with SO_2 gas influences respiratory toxicity.	10 min, 30 min and 1 h	1:100	DI			Batch leaching informed by methods in IVHHN protocol (Stewart et al. 2013). Leachates were filtered through 0.2 μm and 0.45 μm filters for anion and cation analysis, respectively. Cations determined by ICP-MS and anions by IC.

Wygel et al., 2019	Redoubt, Turrialba, Eyjafjallajö-kull, Kilauea	To investigate impacts of ash surface area and bulk composition on leaching rates and subsequent implications for drinking-water contamination.	1 h to 7 days			0.28 ± 0.1 ml/min	Milli-Q water	Leachate solutions were collected every 1 h over a 8 h period, then every 12 h for 4 days, then every 24 h for another 3 days. Cations by ICP-MS, anions by IC.
Damby et al., 2018	Kilauea	To assess health, agricultural and environmental hazards of elements leached from ashfall from Kilauea volcano.	1 h	1:20 and 1:100	DI			Cations determined by ICP-OES and anions by IC. pH and specific conductance of all samples measured. IVHHN protocol followed as per Stewart et al. (2013).
Bosshard-Stadlin et al., 2017	Oldoinyo Lengai	Investigation of natural leaching of natrocarbonatitic lava and 2007-2008 carbonatite/ silicate ash from Oldoinyo Lengai volcano, Tanzania	1 h	1:100	DI			Ash extracts centrifuged for 3 minutes at 5000 rpm and filtered (0.45 µm). F determined by ISE, Cl and SO_4 by IC and cations by ICP-OES.

Cangemi et al., 2017	Etna, Stromboli, Vesuvius, Vulcano, Santorini, Nea Kamini, Milos	To assess health hazards of potentially-toxic elements released from seven Mediterranean volcanoes	1 h	1:100 1:100	DI HCl (0.1 M)			Batch leaching informed by methods described in Witham et al. (2005). Solutions centrifuged at 3500 rpm for 15 minutes and filtered through 0.45 um cellulose filters. Major anions and cations analysed by IC, and trace elements analysed by ICP-MS.
Maters et al., 2017	Eyjafjallajö-kull, Pinatubo, Chaitén, Redoubt	Investigating controls on the release of iron from volcanic ash	168 h	1:500	H_2SO_4 (0.1 M)			Samples were collected at various time intervals to t=168 h and concentrations of dissolved Fe(II) and Fe(III) determined colorimetrically using Ferrozine method. Experiment intended to simulate release of iron under conditions simulating low pH conditions (in acidic surface film) during airborne transport of volcanic ash.
Anda et al, 2016	Sinabung	To characterise chemical properties of fresh ashfall from Sinabung volcano to assess its effect on underlying soil properties	1 h	1:25	NH_4OAc (1 M)			2 g ash was transferred into a leaching column with filter pulp at the bottom and then leached with 50 ml of 1 M NH_4OAc at pH 7.0 for an hour, then the cations (Ca, Mg, K, Na) were measured in the supernatant. pH and conductivity measured in 1:5 ash/water solution.

Cabré et al. 2016	Grímsvötn	To establish geochemical fluxes to the environment	4 h	1:10	DI	0.12 mL/min	Milli-Q water	Batch leaching at 20 rpm; filtered through PVDF syringe filters with tube tips; pH, conductivity monitored with specific electrodes; fluoride by ISE; major and trace elements by HR-ICP-MS. For column leaching, 10 g ash put in 8 cm long column, fractions collected. Ash/water contact time ~150 min.
Karbowska and Zembrzuski 2016	Eyjafjallajö-kull	Sequential extraction study of bioavailability of thallium from Eyjafjallajökull ash in the environment.	16 h	1:40	DI			Community Bureau of Reference (BCR) extraction scheme, including subsequent fractions: 1) water soluble, 2) exchangeable, 3) reducible, 4) oxidizable, 5) residual.
Stewart et al. 2016	Cordón Caulle	Fate and agricultural consequences of leachable elements added to the environment from the 2011 Cordón Caulle Volcanic Complex tephra fall	1 h	1:20 and 1:100 1:100	DI SG (HCl, 0.032 M)			F by ISE and IC, SO_4 and Cl by IC, ICP-MS. Trace elements by ICP-MS and ICP-OES. Modified version of EPA Method 200:8 used to determine total recoverable metals. Extractions included gastric leaches for better estimation of hazards of ingesting ash, and sequential re-extractions for better estimation of less readily-soluble compounds.

D'Addabbo et al., 2015	Etna Popocatépetl	To assess hazards from leachable elements in ash from Etna and Popocatépetl volcanoes for freshwater organisms	30 min to 7 days	1:10	DI Lake water			Leaching of Popocatepetl 2012, Etna 2011 and Etna 2012 ash, using both deionized and lake water. Extracts analysed for pH, ammonia/ammonium, Ca, K, Ca, Mg, Cl, SO_4, and F by IC, and B. Si, Mn, Fe, Hg, As by ICP-OES.
Cronin et al., 2014	Tongariro	Agricultural and human health hazard assessment of volcanic ash from 2012 hydrothermal eruptions of Tongariro volcano, New Zealand	1 h	1:20 and 1:100 1:100	DI SG			F by ISE and IC, SO_4 and Cl by IC, ICP-MS. Trace elements by ICP-MS and ICP-OES. Gastric leach only as 1:100. Extractions were also extended to include gastric leaches for better estimation of hazards of ingesting ash, and sequential re-extractions for better estimation of less readily-soluble compounds.
Stewart et al., 2014	Sinabung	Agricultural hazard assessment of volcanic ash from eruptions of Sinabung volcano, Indonesia	1 h	1:20 and 1:100 1:100	DI SG			F by ISE and IC, SO_4 and Cl by IC, ICP-MS. Trace elements by ICP-MS and ICP-OES. Extractions were also extended to include gastric leaches for better estimation of hazards of ingesting ash, and sequential re-extractions for better estimation of less readily-soluble compounds.

Achterberg et al., 2013	Eyjafjallajökull	Investigation of ocean fertilisation by ash from Eyjafjallajökull eruption				600 mL/minute	Deionized water	Aerosolic volcanic ash from Eyjafjallajökull was sampled using a low volume air sampler. Deionized water was rapidly (in <10 seconds) passed through the filter to assess 'instantaneous' solubility of Fe.
Canion and Landsberger, 2013	Merapi	To establish quantities of toxic elements leached from Merapi ash using synthetic rainwater	18 h	1:20	Synthetic rainwater (distilled water acidified to pH 5.7)			Method was based on EPA TCLP procedure and involved leaching ash with simulated rainwater for 18±2 hours using a rotator at 30±2 rpm. Elements determined were Ni, Sb, As, Cr, Na, Sr, Mn, K, Cs, Rb, Co, V, Ba, Si, Fe, Th, Al, Ti, U and Zn (by ICP-MS).
Damby et al., 2013	Merapi	Assessment of respiratory hazards to human health of tephra deposits from the 2010 Merapi eruption, Indonesia, with implications for occupational exposure by mining of deposits	1 h	1:100	DI			Anions (F, Cl, SO_4) by IC, major elements (Si, Al, Fe, Mg, Ca, Na, K) by ICP-OES, trace metals (As, Cd, Co, Cr, Cu, Ni, Pb and Zn) by ICP-MS

Horwell et al., 2013	Eyjafjallajökull Grímsvötn	Toxicological profiling of ash from the 2010 Eyjafjallajökull and 2011 Grímsvötneruptions, Iceland	1 h	1:100	DI			1:100 in DI water for 1h; Anions (F, Cl, SO_4) by IC, major elements (Si, Al, Fe, Mg, Ca, Na, K) by ICP-OES, trace metals (As, Cd, Co, Cr, Cu, Ni, Pb and Zn) by ICP-MS
Monick et al., 2013	Eyjafjallajökull	Effects of Eyjafjallajökull volcanic ash on innate immune system response and bacterial growth *in vitro*	1.5 h	1:25	DI HNO_3 (0.001 M)			1:25 in deionized water and 0.001 M HNO_3 for 1.5 hours in ultrasonic bath; leachates filtered through 0.45 um cellulose acetate Millipore filter. Analysis for Ti, Al, Fe, Mn, Li, Be, V, Cr, Co, Ni, Cu, Zn, As, Rb, Dr, Mo, Cs, Ba, La, Ce, Yb, Pb, U by ICP-MS.
Olgun et al., 2013	Etna	Possible impacts of ash emissions from Mt Etna on primary productivity in Mediterranean	1 h and 24 h	1:50 and 1:400	Seawater			For release of fixed-N, P and Si, 1 g ash mixed with 50 mL Atlantic seawater for both 1 h and 24 h. Macronutrients analysed by photometry. Trace metal (Fe, Zn, Cu) release followed by voltammetry for ash/seawater ratios of 1/400.

Olsson et al., 2013	Grímsvötn	Physicochemical characterisation of the Grímsvötn, Iceland volcanic ash to assess the impact on humans and the environment				60 mL/hr	Milli-Q water	cc. 12 g of ash in deionized water in a single pass, plug, flow through reactor (contact time 11±2 min); Al, As, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Gd, Hg, Ho, K, La, Li, Lu, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Pr, S, Si, Sm, Sn, Sr, Tb, Ti,Tm, U, V, Yb, and Zn by ICP-SFMS, and ICP-OES; F, Cl, NO_3, SO_4, SO_3, S_2O_3 by IC
Anda and Sarwani, 2012	Merapi	To characterise fresh ashfall to assess its potential as a source of nutrients to agricultural lands	1 h	1:25	NH_4OAc (1 M)			Cations (Ca, Mg, K, Na) measured by AAS. pH and conductivity measured in 1:5 ash/water solution. Soluble S was extracted by $Ca(H_2PO_4)_2$
Damby, 2012	Colima, Merapi, Mt St Helens, Santiaguito, Soufriere Hills, Unzen	To determine the biodurability of volcanic ash in the lungs	4 weeks	1:100	SLF (pH 7.4), ALF (pH 5.5)			Mass of sample was measured before and after experiment and mineral phases quantified. Cations and anions were not measured.
Durant et al., 2012	Chaitén	First investigation of a rhyolitic ash-fall and the environmental	45 min	1:25	DI			SO_4, Cl, and F by IC; Si, Al, Fe, Mg, Ca, Na and K by ICP-OES; Cr, Co, Ni, Cu, Zn, As, Se, Sr, Ag, Cd and Pb by ICP-MS

		effects of associated rhyolitic ash leachates (2008 Chaitén eruption, Chile)						
Hoffman et al., 2012	Arenal, Popocatépetl, Rabaul-Tarvurvur, Sakurajima, Apoyeque	Investigating release of nutrients and potentially toxic elements from volcanic ash in seawater	15 min	~1:375	Coastal seawater			Concentrations of a range of metals (Al, Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn) determined in seawater, and seawater in contact with ash from five different volcanoes. Metals determined by ICP-MS.
Ruggieri et al., 2012a	Chaitén	The environmental geochemical behaviour of the rhyolitic ashes from the 2008 eruption of Chaitén volcano, Chile	4h	1:10	DI	0.24 mL/min	Milli-Q water	10 g of ash in the column experiment in deionized water; analysis for range of elements by ICP-OES and ICP-MS with ISE for F.
Armienta et al., 2011	Popocatépetl	To assess hazards from volcanic fluorine around Popocatépetl volcano, Mexico	2 h	1:25	DI			

Fiantis et al., 2011	Talang	Investigating evolution of ash from 2005 Talang eruption from pristine condition to condition two years afterwards	Continuous leaching for two years	1:20	NH_4OAc (1 M)			pH determined in 1:2.5 slurry of ash and both deionized water and 0.1M KCl. CEC and exchangeable bases determined using standard method (continuous leaching of 5 g soil with 100 mL 1 M NH_4OAc).
Ruggieri et al., 2011	Lonquimay, Hudson, Llaima, Copahue, Chaitén	Determining potential geochemical fluxes from leaching of ashfall from five South American volcanoes	12 h	1:50 1:10	DI Nitric acid (conc.)			Wide range of major and trace elements determined by ICP-MS; F by ISE. Nitric acid strength was not specified but we assume here that concentrated nitric acid was used (as per Ruggieri et al. 2011).
Le Blond et al., 2010	Rabaul	Rapid evaluation of the health hazard of volcanic ash at Rabaul volcano, Papua New Guinea	1 h	1:25	DI			Fe, As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn by ICP-OES, F by IC
Censi et al., 2010	Etna	Trace element behaviour in seawater during Etna's pyroclastic activity in 2001	72-4320 h	1:10	Seawater			Fresh ash samples were rinsed with ultrapure water then kinetic experiments carried out with 50 g ash samples in 500 mL Nalgene bottes containing seawater, with samples removed at times between 72 and 4320 hours. Analysis for V, Cr, Mn, Co, Cu, Pb

Fiantis et al., 2010	Talang	Investigation of acid dissolution of unweathered ashfall deposits from Talang volcano in a warm, humid climate for understanding the geochemical weathering of the volcanic materials	24 h, 10, 30, 60 days	1:20	DI Citric acid Oxalic acid Sulfuric acid Nitric acid (all 0.02 M)			Agitated for 1h at 27°C, and kept at different temperatures of 10, 27 and 40°C for 60 days; supernatants collected after 24h, and 10, 30 and 60 days; cations (Ca, Mg, K and Na) by AAS, P by visible-light spectrophotometer.
Rango et al., 2010a	Not applicable	Extensive water sampling program supported by leaching experiments on main rock types in Main Ethiopian Rift (MER) to investigate known geochemical anomalies of F, As, Mo, B, U	12 months	1:5	DI			Powdered samples of MER rhyolites and their weathered and reworked sediments were leached with for 12 months in a closed system, with shaking at 100 rpm.

Rango et al., 2010b	Not applicable	The leaching behaviour of pyroclastic glassy ash deposits collected in the central MER, with regards to surface and groundwater fluoride pollution				100 mL/hr	Synthetic rainwater (0.005 M $CaCl_2$, pH 5.5)	Raw, coarse and fine fractions of ash leached through polyethylene columns (20 cm x 1.35 cm I.D.) with synthetic rainwater. Analysis for Ca, Mg, Na, K, F, Cl, NO_3, SO_4, acetate and formate by IC.
Ruggieri et al., 2010	Not applicable	Study of elements leached from ancient rhyolitic ash deposits in the northern Argentina, and their hazardous potential	12 h	1:50 1:10	DI Nitric acid (conc.)			Wide range of major and trace elements determined by ICP-MS; F by ISE.
Wang et al., 2010	Kasatochi	Monitoring of ecological response to the 2008 eruption of Kasatochi volcano, Aleutian Islands	5 min	1:20	DI			USGS Field Leach Test: 5min shaking, 10min settling; Unfiltered aliquots analysed for pH and conductivity Ca, K, Mg, Na, Al, Co, Fe, Cu, Ni, Se, Si, Zn by ICM-MS; Cl, F, NO_3, SO_4 by IC. Soil science parameters (CDC, total C, N, P and S, and plant-available N, P, K were analysed in both pyroclastic and pre-eruption soil samples using standard soil science methods.

Jones and Gislason, 2008	Hekla, Mt St Helens, Sakurajima, Galeras, Soufrière Hills, Lascar, Santiaguito	Assessing volcanic ash fertilization potential and the potential of volcanic ash leachates to poison aqueous environments				60 mL/hr	Deionized water, North Atlantic Ocean seawater, Southern Ocean seawater	Flow-through experiments with deionized water (8h) and seawater (8h or 24h); Br, Li, Na, K, Mg, Ca, Sr, Ba, B, Al, Si, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sn, Pb by ICP-AES, NO_2, NO_3, F, Cl, and SO_4 by IC; NH_4 by automated phenate titration.
Duggen et al., 2007	Arenal, Sakurajima, Mt Spurr	Investigating whether subduction zone volcanic ash can fertilise the surface ocean	A few minutes to 1-2 hours	*Not specified*	Low metal Antarctic seawater			Release of metals (Fe, Cu, Zn) and other nutrients (NH_4, PO_4 and Si) determined in situ using anodic stripping voltammetry for metals and photometry for other nutrients.
Primary purpose of study: evaluating potential of ash leachate as proxies for plume chemistry; ash leachates as monitoring tools for volcanic activity; calculations of volatile budgets								
Marumoto et al., 2017	Aso	Investigating relationship between total mercury and water soluble major ions in ash samples, and volcanic activity at Aso volcano	1 h	~1:1000	DI			Total mercury determined by AAS following thermal desorption and gold amalgamation. Water soluble major ions determined by IC.

Primulyana et al., 2017	Sinabung	Relating geochemical datasets, including S/Cl ratios in ash leachates, to activity of Sinabung volcano from 2010 onward to the present	8 h	~1:200	Distilled water at 80°C			The exact ratio of ash to leachant was not specified, but approximately 0.2-0.3 g ash was immersed in distilled water at 80 °C then made up to 50 mL, implying a ratio of approximately 1:200. Only the size fraction <74 µm was used.
Gutierrez et al., 2016	Not applicable	Experimental studies of HCl adsorption onto synthetic volcanic glass of different composition, to better constrain HCl adsorption in volcanic plumes	24 h	1:10	Distilled water			Stirred for 24 hours in closed Erlenmeyer flask; pH adjustment with $NaHCO_3$, Cl determined by titration against 0.1 N $AgNO_3$
Ayris et al., 2014	Not applicable	Mechanism of HCl uptake by volcanic ash; leaching of post-experiment glass powder to extract soluble reaction products formed during the	4 h	1:50	DI			Cl and SO_4 by IC; Al, Fe, Mg, Ca, Na and K by ICP-AES

		experiments						
Miyagi et al., 2013	Sakurajima	Temporal changes in the colour and the amount of leachates of Sakurajima, Japan ash erupted from 1981-2011 for purpose of understanding magma degassing processed near the top of volcanic conduit	2.5 h	~1:50	DI			1:50 in deionized water for 2.5 h (30min in an ultrasonic bath, 2h later recovery of supernatants); Cl, F, SO_4 by IC
Bagnato et al., 2013	Eyjafjallajökull	To investigate the role of volcanic ash in adsorbing and scavenging volcanogenic volatile elements such as sulfur and halogens	2 h	1:25	DI			F, Cl, SO_4, Na, K, Mg, and Ca by IC; Li, B, V, Cr, Fe, Ni, Cu, As, Se, Rb, Sr, Mo, Sb, Cs, Th, U, Pb, Zn, Mn, Ti, Ba, Al, Cu, Co, Cd by ICP-MS.

Bagnato et al., 2011	Stromboli	Investigation of relationship between ash leachate composition at Stromboli volcano, plume chemistry and eruptive activity	2 h	1:25	DI			F, Cl, SO_4, Na, K, Mg, and Ca by IC; Li, B, V, Cr, Fe, Ni, Cu, As, Se, Rb, Sr, Mo, Sb, Cs, Th, U, Pb, Zn, Mn, Ti, Ba, Al, Cu, Co, Cd by ICP-MS
Armienta et al., 2010	Popocatépetl	Use of chemical characteristics of ash leachates as a monitoring tool for volcanic activity	2 h	1:25	DI			Anions (Cl, F, SO_4)
de Moor et al., 2010	Anatahan	Sulfur isotope compositions of pumice and adsorbed on ash of Anatahan volcano, to constrain the sources of sulfur erupted during the 2003 eruption	12 h	1:80	DI			1:80 in deionized water* for 12 h (including 1 h agitation); anions S, Cl and F by IC. 1:40 ratio also used.

de Moor et al., 2005	Anatahan	Evaluation of the 2003 eruption of Anatahan volcano (Mariana Islands) with emphasis on the understanding of degassing mechanisms	12 h	1:80	DI HNO_3 (0.01M)			1:80 in deionized water for 12 h (including 1 h agitation) and 1:80 in 0.01M HNO_3; cations (Ca, Mg, Na, K, Si, AL, Fe, Mn, Cu, Ba) by ICP-OES, anions (P, S, Cl, F) by IC
Primary purpose of study: method development or proposing new or modified methods								
Stewart & Leonard, 2018a	ManaroVoui (Ambae or Lonbenben)	Comparison of IVHHN leaching method with a modified USEPA method	1 h	1:20 and 1:100	DI			For a single ash sample from Manaro Voui volcano, Vanuatu, one split was analysed according to the IVHHN leaching protocol, and another split analysed using a modified version of EPA Method 1312.
Ruggieri et al., 2012b	Chaitén	An optimisation trial using multivariate factorial analysis to design robust batch leaching method for ash hazard characterisation.	1.5,4 and 16 hr	1:10, 1:25 and 1:50	DI			Leaching was carried out at 20 rpm for various combinations of parameters. Elements analysed were SO_4, Cl, Na, Mg, K, V, Co, Si, Al, Mn, Fe, Ca (major elements by ICP-OES and trace elements by ICP-MS and HR-ICP-MS).
Gislason et al., 2011	Eyjafjallajökull	Characterization of Eyjafjallajökull	4-85 min	~1:1000	DI			No agitation

		volcanic ash, suggestion of a protocol for rapid risk assessment						
Hageman, 2007	Not applicable	USGS Field Leach Test protocol, to be used as a fast and effective geochemical characterisation tool	5 min	1:20	DI			Method specifies using 50 g solid and one litre DI, and shaking the bottle for five minutes by hand then syringe filtering through a 0.45 µm nitrocellulose filter.
Primary purpose of study: literature review								
Ayris and Delmelle, 2012	Not applicable	Review of environmental effects of tephra emissions						
Stewart et al., 2006	Not applicable	Review of studies on the effects of volcanic ashfall on water supplies and model for predicting contamination						
Primary purpose of study: other								

Ayris et al., 2015	Mt St Helens	Retrospective, spatial analysis of Mt. St. Helens tephra leachate compositions from previously published studies						
Borisova et al., 2013	Merapi	Petrological, mineralogical and geochemical study of processes responsible for the highly explosive events at Merapi, Indonesia (2010)	28 h	1:18 to 1:24	Distilled Milli-Q water			Ratios between 1:18 and 1:24 in distilled Milli-Q water for 28h; F, Cl, Br, SO_4, NO_3, NO_2 and PO_4 by IC; trace elements by ICP-MS (whole range, including rare earth elements)

Table 3 Extraction methods and equipment used by participating laboratories

	Lab A	**Lab B**	**Lab C**	**Lab D**	**Lab E**	**Lab F**
Extraction vessel	50 mL polycarbonate centrifuge tubes	250 mL glass conical flasks	125 mL HDPE wide mouth bottles	150 mL glass beakers	50 mL polypropylene centrifuge tubes	60 mL LDPE bottles
Agitation method	End-over-end shaker	Table shaker (orbital)	Table shaker (horizontal)	Table shaker (horizontal)	Table shaker (horizontal)	Rotating 180° shaker
Centrifugation speed	5000 rpm	No centrifuging, samples allowed to settle for 15 minutes	4000 rpm	No centrifuging	3800 rpm	No centrifuging, samples allowed to settle for 15 minutes
Centrifugation time	10 minutes		10 minutes		20 minutes	
Filtration method	Vacuum filtration	Syringe filtration	Syringe filtration	Vacuum filtration	Syringe filtration, 10 mL Injekt syringe attached to 25 mm Acrodisc syringe filter	Syringe filtration
Filters used	0.45 µm	0.45 µm nylon	0.45 µm nylon	0.45 µm nylon	0.2 µm GHP glass	0.45 µm SFCA

	nitrocellulose	filters for cations, 0.2 µm nylon filters for anions	filters for cations, 0.2 µm nylon filters for anions	nitrocellulose	fibre membrane	membrane
Further details	0.4 g of ash to 40 mL leachant for 1:100; 2 g ash to 40 mL leachant for 1:20		1 g ash to 100 mL water for 1:100; 5 g ash to 100 mL water for 1:20. Extracts diluted 1:10 prior to ICP-MS analysis.		0.4 g of ash to 40 mL leachant for 1:100; 2 g ash to 40 mL leachant for 1:20. Extracts diluted 1:100 prior ICP-MS analysis.	0.4 g of ash to 40 mL leachant for 1:100; 2 g of ash to 40 mL leachant1:20. No dilution.

Table 4 Instrumental determination of elements in deionized water (DI) and simple gastric (SG) leach extracts by different laboratories (SG in parentheses), n.a. is 'not analysed'.

	Lab A	**Lab B**	**Lab C**	**Lab D**	**Lab E**	**Lab F***
Anions						
Chloride	IC	IC	IC	ISE	IC	IC
Fluoride	ISE	IC**(**ISE**)**	IC	ISE	IC	IC
Sulfate	IC	IC	IC	Turbidimetry	IC	IC
Bromide	IC	IC	IC	n.a.	n.a.	IC
Nitrate	IC	IC + FIA	IC	IC	IC	IC
Cations major						
Calcium	ICP-MS	ICP-OES	ICP-MS	AAS	ICP-OES	ICP-OES
Magnesium	ICP-MS	ICP-OES	ICP-MS	AAS	ICP-OES	ICP-OES
Sodium	ICP-MS	ICP-OES	ICP-MS	AAS	ICP-OES	ICP-OES
Potassium	ICP-MS	ICP-OES	ICP-MS	AAS	ICP-OES	ICP-OES
Aluminium	ICP-MS	ICP-OES	ICP-MS	n.a.	ICP-OES	ICP-MS
Cations minor						
Arsenic	ICP-MS	ICP-OES	ICP-MS	n.a.**(**HG-AAS)	ICP-MS	ICP-MS

Barium	ICP-MS	ICP-OES	ICP-MS	n.a.	ICP-MS	ICP-MS
Boron	ICP-MS	ICP-OES	ICP-MS	UV-Vis	ICP-MS	ICP-MS
Cadmium	ICP-MS	ICP-OES	ICP-MS	n.a.(AAS)	ICP-MS	ICP-MS
Chromium	ICP-MS	n.a.	ICP-MS	n.a.(AAS)	ICP-MS	ICP-MS
Cobalt	ICP-MS	n.a.	ICP-MS	n.a.	ICP-MS	ICP-MS
Copper	ICP-MS	ICP-OES	ICP-MS	AAS	ICP-MS	ICP-MS
Iron	ICP-MS	ICP-OES	ICP-MS	AAS	ICP-OES	ICP-MS
Lead	ICP-MS	ICP-OES	ICP-MS	n.a.(GF-AAS)	ICP-MS	ICP-MS
Lithium	ICP-MS	ICP-OES	ICP-MS	n.a.	ICP-MS	ICP-MS
Manganese	ICP-MS	ICP-OES	ICP-MS	AAS	ICP-MS	ICP-MS
Molybdenum	ICP-MS	n.a.	ICP-MS	n.a.	ICP-MS	ICP-MS
Nickel	ICP-MS	ICP-OES	ICP-MS	n.a.(AAS)	ICP-MS	ICP-MS
Selenium	ICP-MS	n.a.	ICP-MS	n.a.	ICP-MS	ICP-OES
Silicon	n.a.	ICP-OES	ICP-MS	UV-Vis	ICP-OES	ICP-MS
Strontium	ICP-MS	ICP-OES	ICP-MS	n.a.	ICP-MS	ICP-MS
Titanium	n.a.	n.a.	ICP-MS	n.a.	ICP-MS	ICP-MS
Zinc	ICP-MS	ICP-OES	ICP-MS	AAS	ICP-MS	ICP-MS

*Lab F did not return data for the simple gastric leach.

FIA: Flow-injection analysis

IC: Ion chromatography

ISE: Ion-selective electrode

ICP-MS: Inductively-coupled plasma mass spectrometry

ICP-OES: Inductively-coupled plasma optical emission spectrometry

AAS: Atomic absorption spectroscopy

UV-Vis: Ultraviolet–visible spectroscopy

HG-AAS: Hydride generation atomic absorption spectroscopy

GF-AAS: Graphite furnace atomic absorption spectroscopy

Table 5 Between-laboratory mean analyte concentrations for deionized water leach at 1:20 and 1:100 extraction ratios. All concentrations in mg/kg ash.

	Mean analyte concentrations (mg/kg) for the six laboratories at different extraction ratios, ± standard deviations		
	1 to 20	1 to 20 minus Lab B[1]	1 to 100
SO_4	1337±260	1429±97	1476±93
Ca	554±98	592±36	620±30
Cl	291±26	300±11	296±42
Na	145±16	151±7	158±12
Mg[2]	32±3[a]	33±2[a]	39±8[b]
F	12±4	13±0.7	16±5
Mn	10.2±1.2	10.7±0.5	11.5±1.3
K	9.0±2.0	9.4±2.0	12±5
Sr	3.0±1.0	3.3±0.3	3.3±0.3
Al	1.3±0.6	1.4±0.6	1.4±0.6
Cu[2]	1.0±0.2[a]	1.1±0.2[a]	1.6±0.3[b]
Ba	0.7±0.2	0.8±0.1	0.8±0.2
Zn	0.43±0.18	0.46±0.19	1.3±1.4
B	0.2±0.1		0.5±0.5
Li	0.058±0.005		0.065±0.007
Co	0.030±0.002		0.031±0.001
Ni	0.02±0.01		0.04±0.05

[1] 1:20 results for lab B omitted. Where there are blank cells, lab B did not report data for this element or concentrations were below detection limits.

[2] T tests (one-tailed, with two-sample equal variance) were run to compare 1:20 means (with and without lab B data included) with 1:100 means across the six laboratories. Statistical differences were found only for copper and magnesium. Superscripts a and b denote statistically different data sets.

Table 6 Between-laboratory mean analyte concentrations for 1:100 deionized (DI) water and simple gastric (SG) leaches. All concentrations in mg/kg ash. Standard deviations are only calculated for elements where at least four of the six laboratories reported concentrations above detection limits.

	1:100 deionized water	1:100 simple gastric	SG/DI ratio
	mg/kg		
Fe	0.4	146	365
Al	1.4±0.6	479±115	331
As	0.006	0.22±0.03	37
Cu	1.6±0.3	13±2	8.4
F	16±5	39±8	2.4
Co	0.031±0.001	0.07±0.01	2.3
Cd	0.0035	0.008	2.3
Mn	11.5±1.3	22±6	1.9
Ni	0.04±0.05	0.04	1.1
Zn	1.3±1.4	1.3±1.1	1.0
Pb	<0.0003	0.24±0.08	-
Cr	<0.001	0.01	-

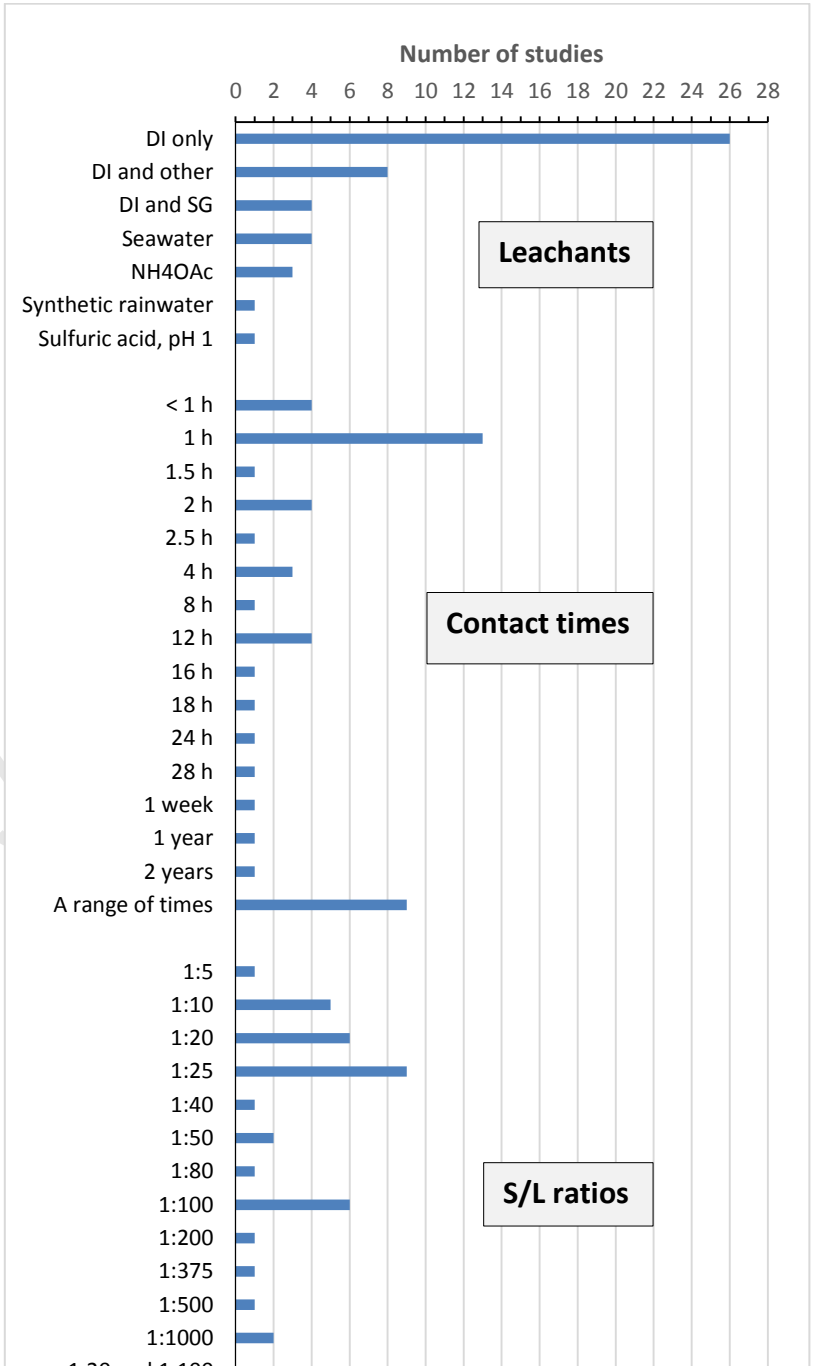
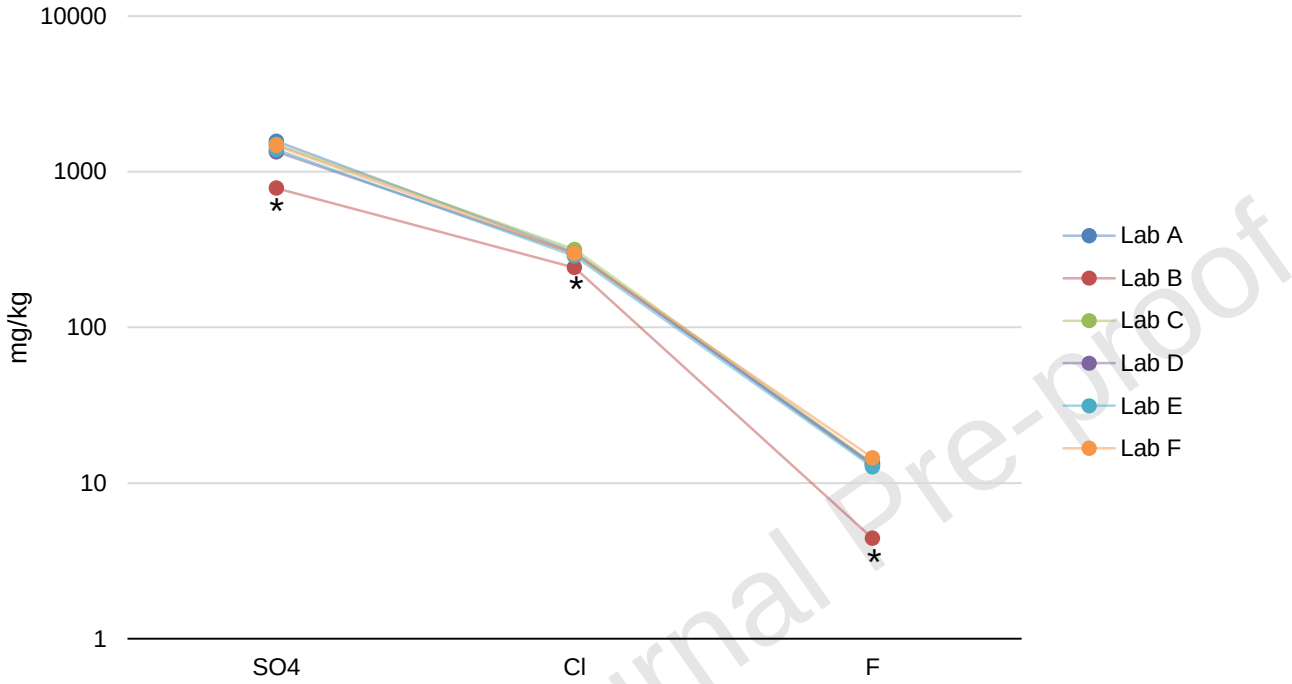

Number of studies
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28
DI only
DI and other
DI and SG
Seawater
NH4OAc
Synthetic rainwater
Sulfuric acid, pH 1
Leachants
< 1 h
1 h
1.5 h
2 h
2.5 h
4 h
8 h
12 h
16 h
18 h
24 h
28 h
1 week
1 year
2 years
A range of times
Contact times
1:5
1:10
1:20
1:25
1:40
1:50
1:80
1:100
1:200
1:375
1:500
1:1000
S/L ratios

Figure 1 Overview of leaching parameters **(**leachants, contact times and solid-to-liquid (S/L) ratios) used in ash leachate studies published from 2005 to 2019. Additional information on each study is provided in Table 2.

A



B

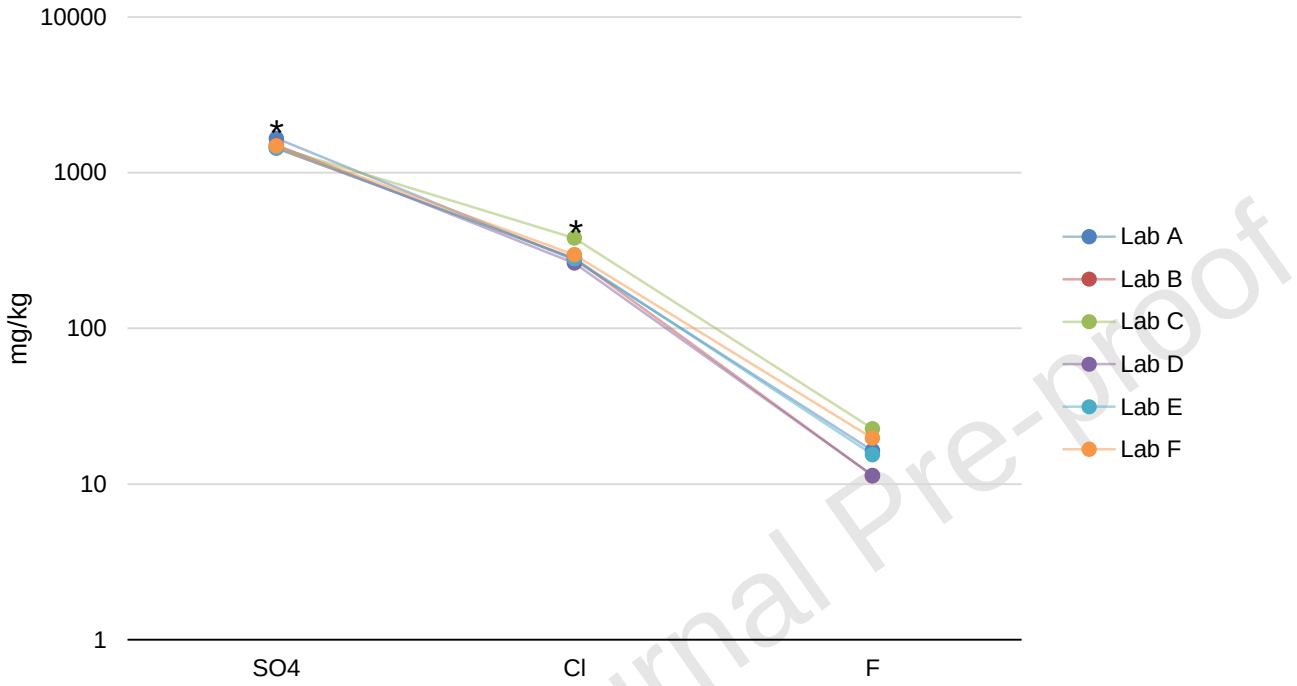
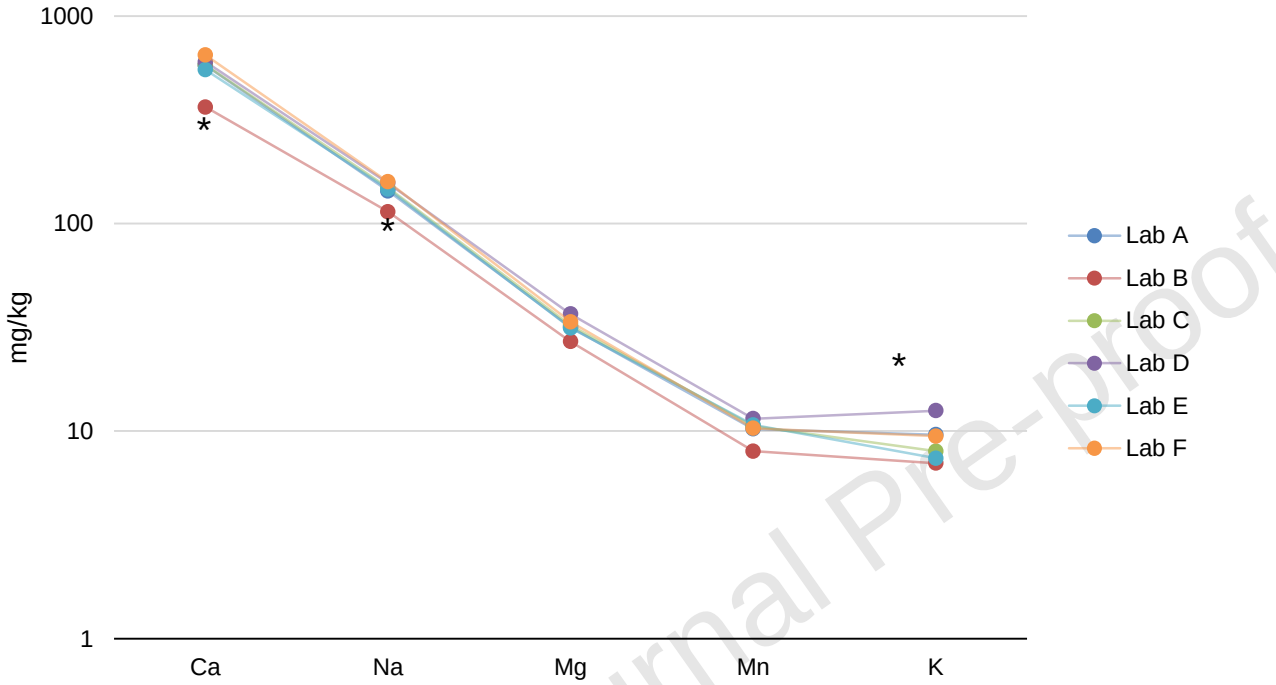


Figure 2: Water-extractable anions at ratios of (A) 1:20 and (B) 1:100. Data are reported as mg element per kg of ash (dry weight basis). Each point is the mean of three replicates for each laboratory. Error bars are the standard error of the mean. Where error bars are not visible, they are less than the size of the symbol. Asterisks identify points determined to be outliers by modified Z-score statistics.

A



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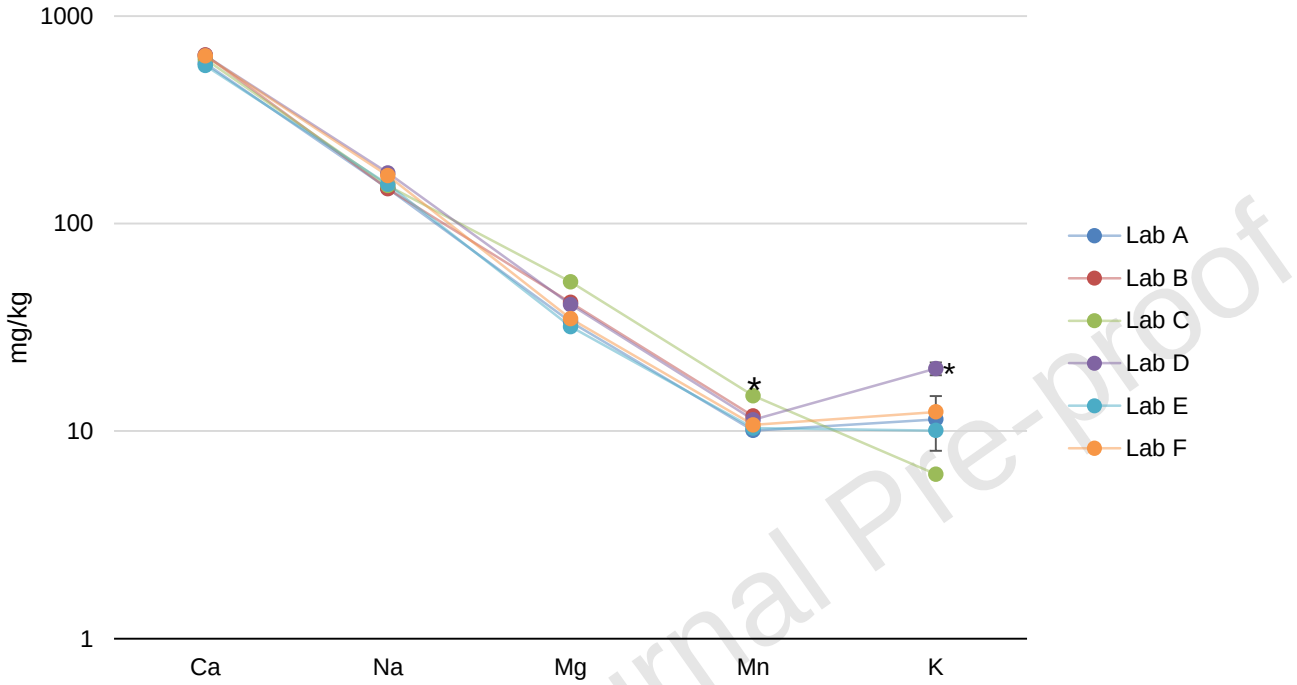
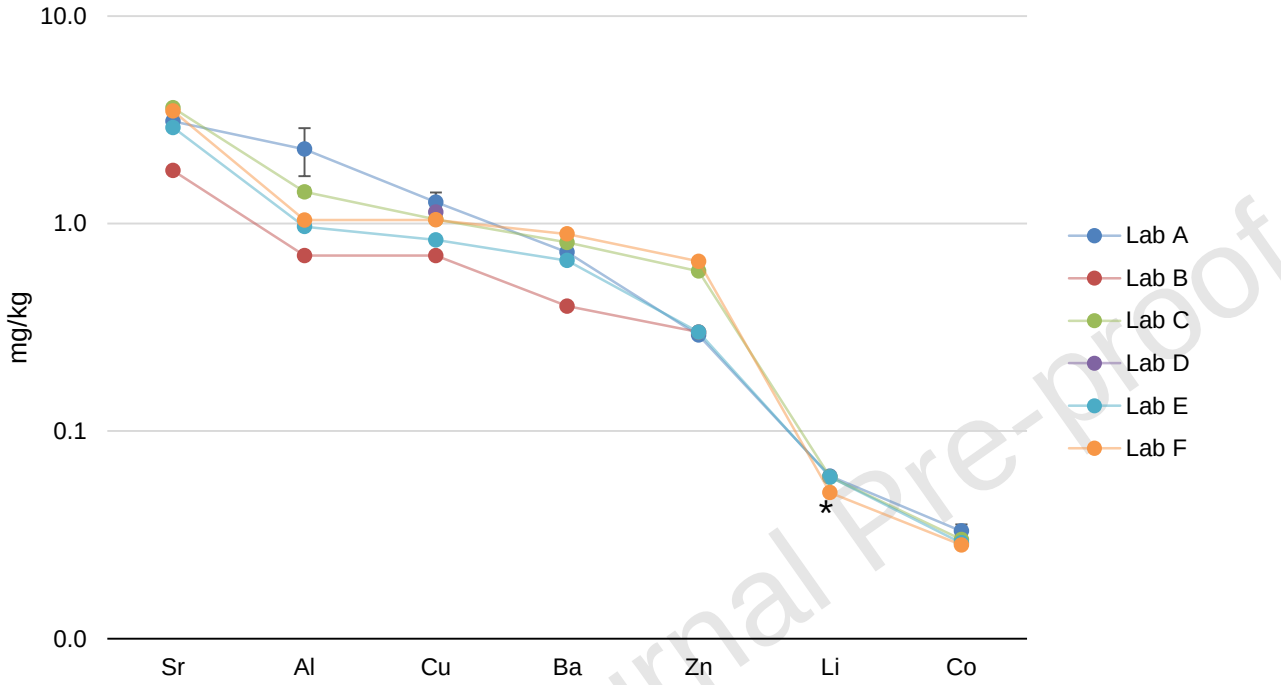


Figure 3: Water-extractable major cations at ratios of (A) 1:20 and (B) 1:100. Data are reported as mg element per kg of ash. Each point is the mean of three replicates for each laboratory. Error bars are the standard error of the mean. Where error bars are not visible, they are less than the size of the symbol. Asterisks identify points determined to be outliers by modified Z-score statistics.

A



B

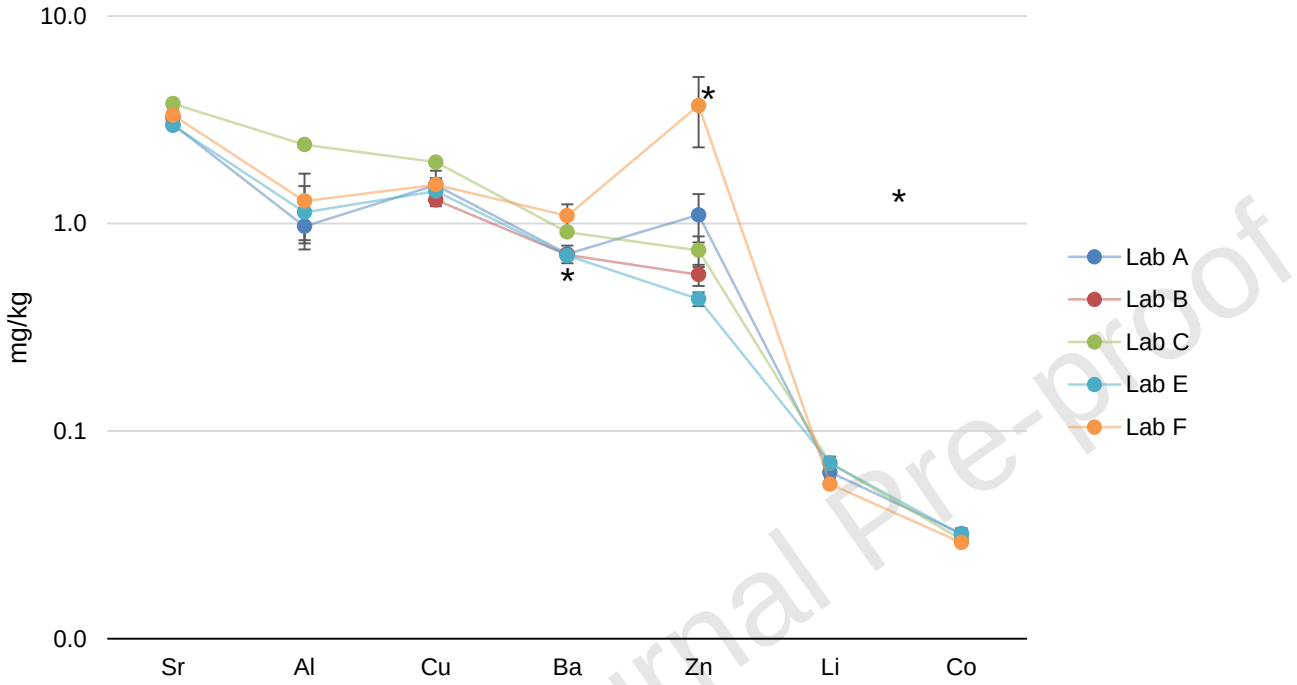


Figure 4: Water-extractable minor elements at ratios (A) 1:20 and (B) 1:100. Analytes for Lab D at 1:100 were either not attempted or were below detection limits. Data are reported as mg element per kg of ash. Each point is the mean of three replicates for each laboratory. Error bars are the standard error of the mean. Where error bars are not visible, they are less than the size of the symbol. Asterisks identify points determined to be outliers by modified Z-score statistics.

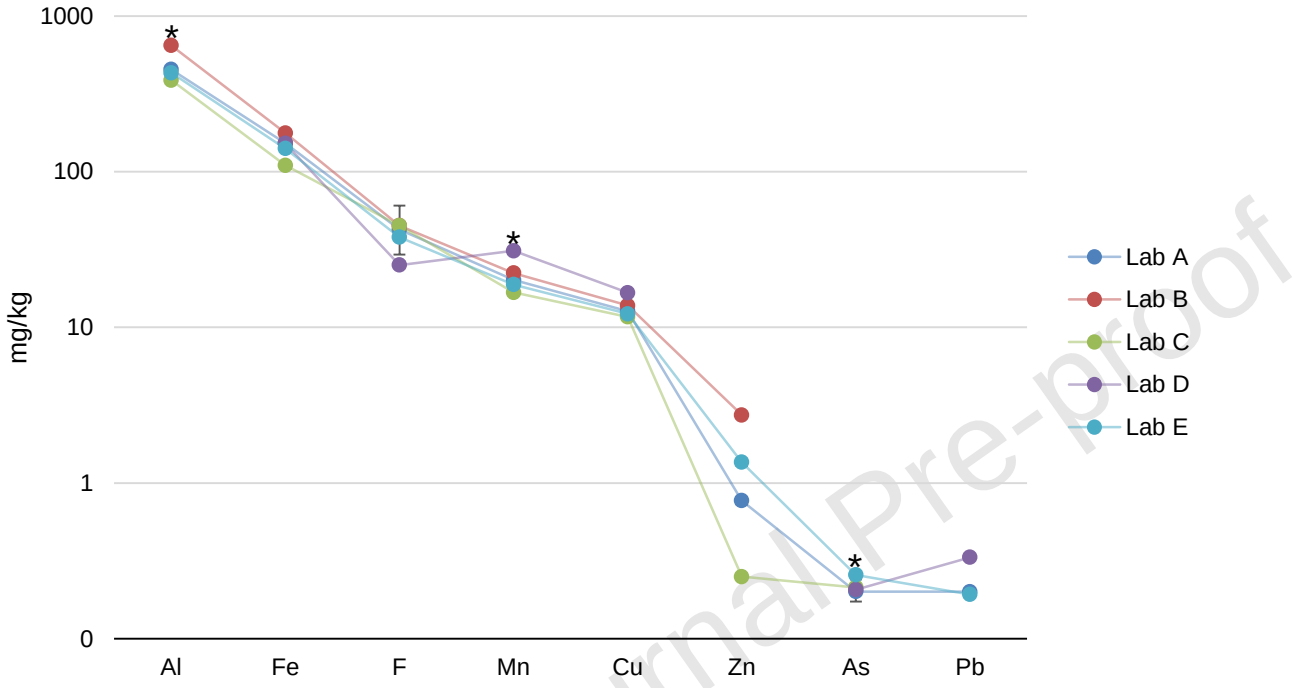


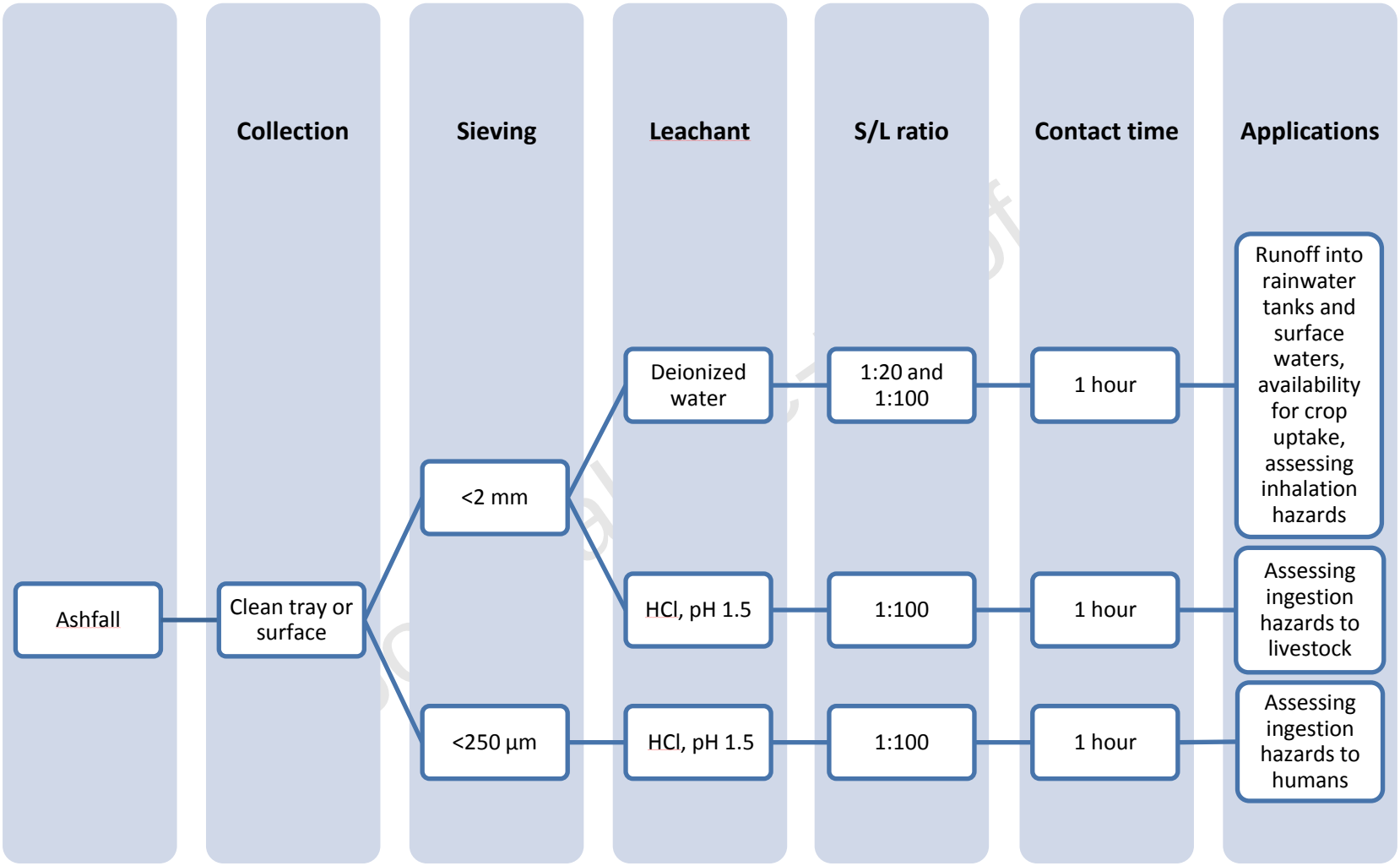
Figure 5: Simple gastric-extractable minor elements at 1:100. Lab F did not report data for the simple gastric leach. Data are reported as mg element per kg of ash. Each point is the mean of three replicates for each laboratory. Error bars are the standard error of the mean. Where error bars are not visible, they are less than the size of the symbol. Asterisks identify points determined to be outliers by modified Z-score statistics.

AUTHOR STATEMENT FOR VOLGEO_2019_281

All authors: Writing – review and editing. **Carol Stewart**: Conceptualization; Data curation; Investigation; Methodology; Project administration; Writing original draft. **David Damby:** Investigation, Data curation, Writing original draft. **Ines Tomasek**: Investigation, Data curation. **Claire Horwell**: Conceptualization; Funding acquisition. **Geoffrey Plumlee**: Investigation; Supervision; Funding acquisition. **Maria Aurora Armienta**: Investigation. **Maria Gabriela Ruiz Hinojosa**: Investigation. **Moya Appleby**: Investigation. **Pierre Delmelle:** Investigation, Supervision. **Shane Cronin.** Methodology; Supervision. **Christopher Ottley**: Investigation. **Clive Oppenheimer**: Investigation. **Suzette Morman**: Investigation.

CONFLICT OF INTEREST STATEMENT FOR VOLGEO_2019_281

All authors declare no conflicts of interest.


Collection
Sieving
Leachant
S/L ratio
Contact time
Applications
Ashfall
Clean tray or surface
<2 mm
<250 µm
Deionized water
HCl, pH 1.5
HCl, pH 1.5
1:20 and 1:100
1:100
1:100
1 hour
1 hour
1 hour
Runoff into rainwater tanks and surface waters, availability for crop uptake, assessing inhalation hazards
Assessing ingestion hazards to livestock
Assessing ingestion hazards to humans

Graphical abstract

Research highlights

- Using different leachate analysis methods has hindered the creation of a global database
- We propose a standardized protocol for ash leachate analysis
- We carry out an interlaboratory comparison study to validate this protocol
- Results indicate good comparability for most parameters measured
- Spatially and temporally-representative sampling of ash deposits is also required